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ABSTRACT

THERMOCHEMICAL PROPERTIES OF C3 TO C5 UNSATURATED CARBONYL ALKENES: ENTHALPIES OF FORMATION, ENTROPY, HEAT CAPACITY, BOND ENTHALPY

by
Ruiqi Jian

α,β and $\alpha\text{-}\gamma$ unsaturated carbonyl compounds are important classes of carbonyl compounds with the general structure $R\text{-(O=C)-C}^\alpha\text{=C}^\beta\text{-R}'$ and $R\text{-(O=C}^\gamma\text{)-C}^\beta\text{-C}^\alpha\text{=C}^\beta\text{-R}'$. These compounds are utilized in industry and are also produced as intermediates of hydrocarbon oxidation in chemistry of the atmosphere and in combustion. These unsaturated carbonyls are common environmental pollutants, are frequently associated with adverse effects, and are considered to play an important role in human cancer. Their stability, thermochemical properties are important to understanding their reaction paths in atmospheric, combustion and bio related environments. Enthalpy, entropy, and heat capacity of unsaturated alkene molecules, and radicals corresponding to hydrogen atom loss from the parent stable molecules are determined in this study. Structures and enthalpies of formation ($\Delta_f H^\circ_{298}$) are determined for series of unsaturated carbonyl hydrocarbons and their carbon centered radicals at B3LYP/6-31g(d,p), CBS-QB3 and M062X/6-31+G(d,p) theory levels by using the isodesmic reactions approach. Entropy(S°) and heat capacities ($C_p(T)$), and the contributions from vibrational, translational and external rotational are calculated using the rigid-rotor-harmonic oscillator approximation, based on the vibration frequencies and structures obtained from density functional studies. Potential barriers for internal rotors in each molecule are determined and used to calculate contributions to S° and $C_p(T)$ from the hindered rotors. $\Delta_f H^\circ_{298}$ for unsaturated carbonyl alkenes are, $\text{CH}_2\text{=CHCH=O}$, 16.89 kcal/mol, $\text{CH}_3\text{CH=CHCH}_2\text{CH=O}$ (trans),

27.41 kcal/mol, $\text{CH}_2=\text{CHCH}_2\text{CH}=\text{O}$, 19.91 kcal/mol. The trans conformation of $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}=\text{O}$ is more stable than cis form. For a C-H bond on allylic adjacent to carbonyl group, the allylic has resonance with the carbonyl group. Several bond enthalpies are quite different from that normally found on olefins, and carbonyls. The bond enthalpy for the secondary C-H bonds, adjacent to carbonyl group, are quite low: 77.0 kcal/mol for $\text{CC}=\text{CC}(-\text{H})\text{C}=\text{O}$ and 77.8 kcal/mol for $\text{C}=\text{CC}(-\text{H})\text{C}=\text{O}$. The C-H bond enthalpy at the position of secondary vinyl, adjacent to carbonyl group, $\text{C}=\text{C}(-\text{H})\text{C}=\text{O}$ shows a value of 113.1 kcal/mol, which is about 5 kcal/mol higher than a normal secondary vinyl C-H bond. The C-H bond enthalpy of the primary vinyl of cdccdo is increased but only by 0.7 kcal/mol from a normal primary.

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Ruiqi Jian

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in Partial Fulfillment of the Requirements for the Degree of
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APPROVAL PAGE

**THERMOCHEMICAL PROPERTIES OF C3 TO C5 UNSATURATED
CARBONYL ALKENES: ENTHALPIES OF FORMATION, ENTROPY, HEAT
CAPACITY, BOND ENTHALPY**

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TO MY PARENTS, WITH LOVE

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CHAPTER 1

INTRODUCTION

α,β -unsaturated carbonyl compounds are an important class of carbonyl compounds with the general structure $-(O=C)-C^\alpha=C^\beta-$. The α,β -unsaturated carbonyl moiety is present in a large number of natural and synthetic products exhibiting a variety of biological properties.¹ The epoxidation reactions of unsaturated carbonyl compounds are widely applied and highly valuable to industry in the synthesis of intermediates in pharmaceutical and fine chemicals. The very high value dictates the reason that the reactions of these species are widely studied with focus of improving their reaction selectivity, which in general is not high. Many research works have focused on their epoxidation reactions to improve and / or achieve selectivity.²

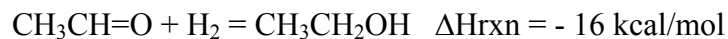
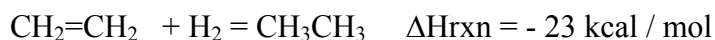
These unsaturated carbonyl compounds are also used in as solvents including paint thinners and additives, nail polish removers, food additives, disinfectants, and dental restorative materials. They are routinely observed in hydrocarbon analysis of air in tropospheric environments. They are also formed from oxidation of unsaturated hydrocarbons, for example, 1-butenal can be formed from reaction of butadiene with OH radical.



$$\Delta H_{\text{rxn}} = - 2 \text{ kcal/mol}$$

Chemo-selective hydrogenation of compounds containing both C=C and C=O groups is one of the most fundamental molecular transformations described in textbooks. Hydrogenation of C=C bond is relatively easier than hydrogenation of a C=O bond

because: (a) thermodynamics favors the hydrogenation of the olefin $\text{CH}_2=\text{CH}_2$ bond over that of the carbonyl bond $\text{CH}_2=\text{O}$.

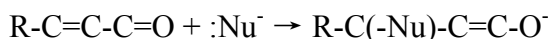


and



(b) Kinetic reactivity also favors reactivity of the olefin group, it is harder to react the carbonyl group because the $\text{C}=\text{O}$ π bond is ~ 20 kcal/mol stronger than the $\text{C}=\text{C}$ π bond and of an olefin $\text{C}=\text{C}$; and it is harder to attack the carbonyl bond.³

α,β -Unsaturated carbonyls also possess a more strongly polarized carbon -oxygen double bond due to the presence of an adjacent double bond between α carbons and β carbons. In these compounds the carbonyl group draws electrons away from the alkene, and is conjugated with an alkene, which makes it even more reactive than simple carbonyls. Unlike the case for simple carbonyls, α,β -unsaturated carbonyl compounds are often attacked by nucleophiles at the β carbon.



Since α,β -unsaturated compounds are electrophiles, many of them are toxic, mutagenic and carcinogenic.

For unsaturated carbonyls like butenal ($\text{CH}_2=\text{CHCH}_2\text{CHO}$) and 2-pentenal ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{CHO}$) there is a sp^2 CH_2 group between the carbonyl and the olefin groups. These CH_2 groups have weak C-H bond because of resulting resonance of the electron remaining on the carbon after loss of the $\text{H}\cdot$ atom with the olefin and with the

carbonyl. These weak C-H bonds are readily attacked by radicals like OH and other species in the radical pool. Once these resonantly stabilized radicals are formed the radical site reactions with molecule oxygen O₂ are slow, as the R-OO• bonding is not strong due to loss of resonance.

An ultimate goal of this research is to study the reactions of these stabilized intermediates with O₂; as these radicals are readily formed via in atmospheric and combustion processes are on a relative scale to other radicals they are stable or less reactive. They have longer lifetimes due to the stability from resonance and thus may have a significant presence in these chemical systems.

Thermochemical parameters for only a few of these unsaturated carbonyl compounds have been reported in the literature. Enthalpy of formation, entropy, and bond of energy data for 2-propenal are reported by Li, Bear, Asatryan, da Silva⁴, Benson, Rutz, Bozzelli⁵, Alfassi, Golden⁶, and Goldsmith⁷. 2-propenal serves as a model compound for methacrolein (CH₂=C(CH₃)CH=O) and methyl vinyl ketone, (CH₂=CHC(=O)CH₃) because of its specific formation. Compare to 108 kcal/mol bond strength of CH₂=C(-H)CH₃, C=C-CH(-H)CH=O has bond strength of 77.8 kcal/mol as a result of conjugation of the odd carbon electron with the π bond systems of the carbonyl and / or the olefin. This is a very significant difference.

The value of enthalpy of formation for 2-propenal $\Delta_f H^\circ_{298} = -16.5 \pm 2.4$ kcal/mol was reported by Li and Bear.⁴ In the earlier literature, Alfassi and Benson⁶ used group additivity to estimate $\Delta_f H^\circ_{298} = -17.7$ kcal/mol; there is also a reference reported $\Delta_f H^\circ_{298} = -17.8$ kcal/mol cited by Asatryan, da Silva and Bozzelli. It is apparent from surveys that the 2-propenal enthalpy of formation likely lies in the range of -14.0 to -19.0 kcal/mol.⁴

A standard enthalpy, entropy for the radical $\text{CH}_2=\text{CHC}\cdot\text{O}$ are 21.9 kcal/mol, 68.0 cal/mol/K by Rutz, da Silva, and Bozzelli.⁵ An older value for the C-H bond enthalpy for this radicals is 87.1 ± 1.2 kcal/mol by Alfassi and Golden⁶ and in more recent literature by Goldsmith et al⁷, report a value of 23.2 kcal/mol for the enthalpy of formation. Goldsmith⁷ also reports entropy and heat capacity for 2-propenal and all corresponding radical.

In this study, the thermochemistry of three stable (parent) molecules and their allylic, carbonyl and vinylic carbon radicals are determined. Enthalpies of formation, C-H bond energies, entropy and heat capacity for parent molecules 2-propenal $\text{CH}_2=\text{CHCH}=\text{O}$ (cdccdo), 3-butenal $\text{CH}_2=\text{CHCH}_2\text{CH}=\text{O}$ (cdcccdo), 3-pentenal $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}=\text{O}$ (cccccdo), and their radicals are studied using several different methods in computational chemistry. Comparison of the thermochemical properties with literature values are presented and analyzed. This study also calculated the bond dissociation enthalpies of the allyl, carbonyl and vinyl C-H bonds, in order to evaluate if the levels of stabilization in corresponding radicals. The thermochemical parameters are needed in order to evaluate, reaction paths and kinetic processes of parent molecules and radicals in atmospheric (troposphere) and in combustion environments. These values also provide a base for estimation of barriers for abstraction of the resulting resonantly stabilized C-H bond by radical specie. Equilibria and energies for simple C-H and C-C bond dissociation reactions are important to understand reaction paths and chemistry of these unsaturated aldehydes.

CHAPTER 2

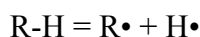
COMPUTATIONAL METHODS

All structure and absolute energy (enthalpy) calculations are performed using the Gaussian 09 program suites⁴ and structures are drawn using the GaussView application.⁸ Geometries for the parent molecules and radicals are initially calculated at the B3LYP/6-31G(d,p) level. There is a general consensus that B3LYP methods provide excellent low-cost performance for structure optimizations.⁸ The B3LYP/6-31G level of theory is indicated to be one of the most reliable computational methods for optimization geometries of small polar compounds as well as being widely used for the calculation of radical species. Optimized geometries, vibrational frequencies for molecules and related radical species are then calculated at B3LYP/6-31G level of the theory.⁹ To identify and verify the lowest energy conformation of each molecule and radical, potential energy curves for the internal rotation barriers at B3LYP/6-31G(d,p) level of theory are calculated.

CBS-QB3 is a multilevel model that combines the results of several ab initio and density functional theory individual methods and empirical correction terms to predict molecular energies with high accuracy and relatively low computational cost.¹⁰ It is a complete basis set method that uses geometries and frequencies from the B3LYP, specifically B3LYP/6-31G(2d,d,p) level followed by single point energy calculations at the CCSD(T), MP4SDQ, and MP2 levels.¹¹ The M062X functional is a high non-locality density functional theory with double amount of nonlocal exchange (2x).¹²

Isodesmic reactions are implemented to accurately calculate enthalpy of formation and bond enthalpies for parent molecules and stable species, using the enthalpies from B3LYP/6-31G(d,p), CBS-QB3 and then M062X/6-31+G(d,p) level. Isodesmic reactions are hypothetical reactions which incorporate similar bonding environments for both reactants and products that allows for cancellation of error associated with each method of analysis.

The C-H bond enthalpies are derived using the bond cleavage reaction,



where R=H and R• are both calculated and H atom uses the established standard enthalpy of 52.1 kcal/mol.

Contributions to the entropy and the heat capacity from translation, vibrations and external rotation, optical isomers, and symmetry are calculated using the “SMCPS” program.¹³ Contributions from hindered internal rotors to S° and Cp(T) are determined using “VIBIR” program.¹⁴ The VIBIR program utilizes the method of Pitzer and Gwinn. In the theory, there is no adjustment for coupling of internal rotor motion with vibration; the rotational groups are assumed symmetrical which is accurate for the primary and terminal methyl group rotation in isomers. The reduced moments of inertia are calculated based on the optimized geometries using the mass and radius of rotation for the rotational groups.²⁰

Notation

Throughout this article, abbreviations utilized in molecule names are: “d” presents a double bond; “j” or “•” represents a radical site on the preceding carbon atom.

CHAPTER 3

RESULT AND DISCUSSION

3.1 Selection of Low Energy Conformer: Internal Rotor Potential Analysis

Rotational conformer energies are calculated to determine the lowest energy conformation of each molecule and radical and to identify the barriers to torsional motion. The intramolecular torsional motion, an internal rotor contributes to entropy and heat capacity of the molecular and radical. Internal rotor potential energy curves are calculated and used to determine internal rotation barriers, symmetries (folds) and the lowest energy structures. The barriers and moments of inertial are used to determine the entropy and heat capacity contributions using the VIBIR program and the method of Pitzer and Gwinn.

The B3LYP/6-31G(d,p) level of theory is used to determine the enthalpy as a function of the dihedral angles in each of the molecules and radicals. The torsion angles are scanned between 0° and 360° in steps of 14° , to determine the lowest energy geometries. If lower energy geometry is found, the new geometry is set and all dihedral scans repeated to ensure the lowest energy conformation.

The resulting potential energy barriers for internal rotations in the stable parent and radical molecules are illustrated in Figures A.1-A.3. The geometries of the lowest energy structures are illustrated in Figure 3.1. The optimized Z-Matrix for parent unsaturated carbonyl alkene and radicals from CBS-QB3 level are listed in Table B.1.

- All of the terminal methyl groups adjacent to vinyl group ($\text{CH}_3\text{-CH=CH-}$) for parent unsaturated carbonyl alkene and radicals, exhibit three fold symmetry with energy barriers between 1 and 2 kcal/mol.

- All internal rotors between a carbonyl group and a secondary carbon (CHO--CH₂-) for parent molecules and radicals exhibit three folds and barrier energies between 0.5-3 kcal/mol.
- The fold number decrease from three to two symmetry folds, and the fold barrier energy for carbonyl increases to 8.5-9.5 kcal/mol when carbonyl adjacent to vinyl group (CHO--C=C-).
- When the radical site is on carbonyl group, the barrier fold number for internal rotor between carbonyl group and secondary (C•O--CH₂-) is two and the barrier energies are low at 1 to 2 kcal/mol. When radical site on secondary adjacent to carbonyl group, the internal rotor between radical site and vinyl group (CHO-C•--C=C-) have barriers over 10 kcal/mol; this is because of the radical formation have the resonance with the carbonyl group.

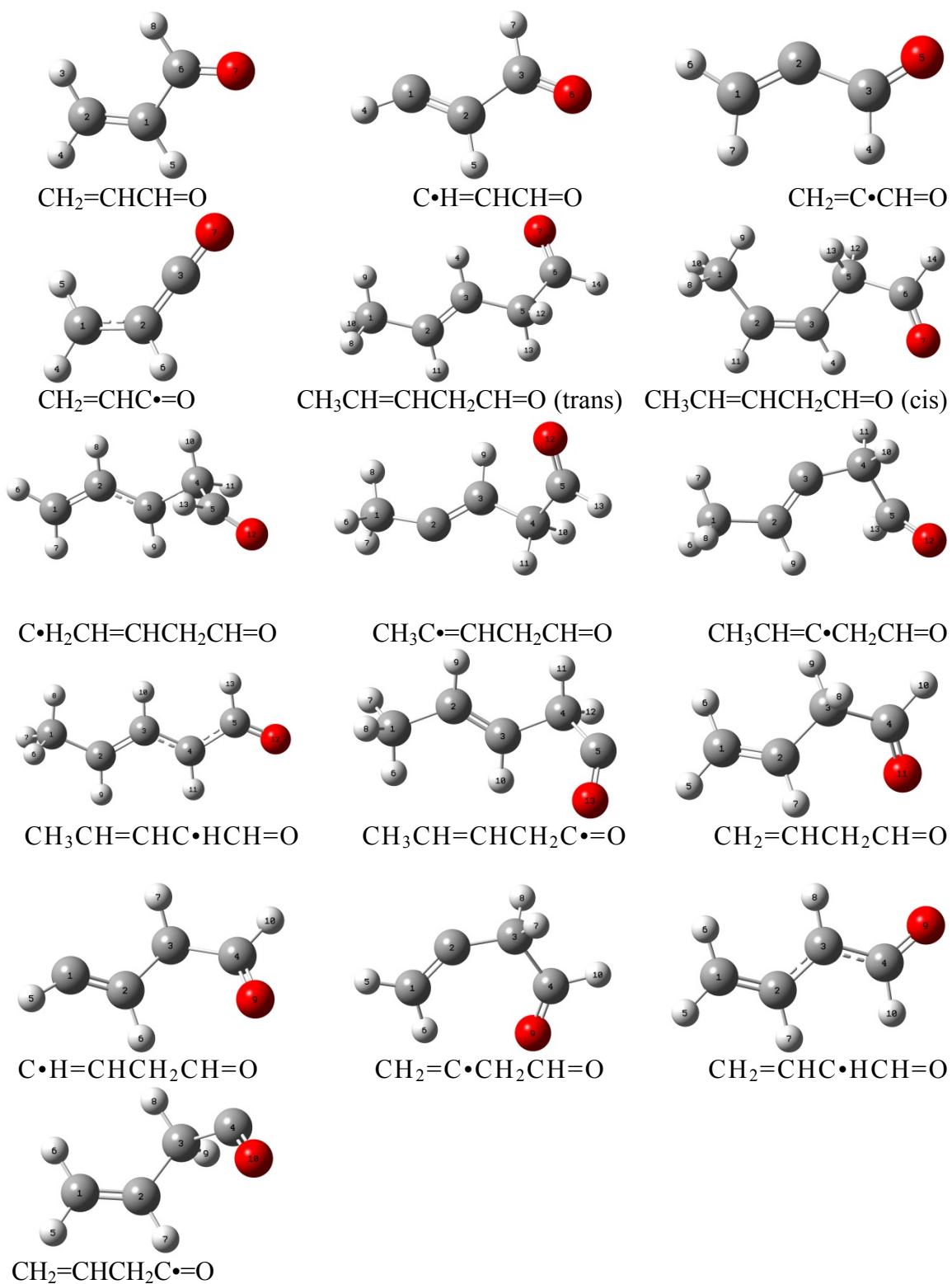


Figure 3.1 Geometry of the Lowest Energy Conformer of the Parent Molecules and the Radicals.

3.2 Enthalpies of Formation

Enthalpies of formation of the parent molecules have been determined using corresponding $\Delta H_{\text{rxn}298}$ from the calculated enthalpies of each species in each of the isodesmic work reactions and calculated enthalpies of each species. $\Delta_{\text{rxn}}H^{\circ}_{298}$ are calculated at the B3LYP/6-31G(d,p), CBS-QB3 and M062X/6-31+G(d,p) level.

Density Functional Theory (DFT), as noted earlier is considered to have relative very good accuracy for structure and moderate accuracy for structure.¹⁵ DFT performs a less accurate calculation of energies, because these calculations usually start with a molecule that have a closed shell of electrons and when the molecule breaks into two or more fragments that are open shell molecules (radicals). The energy difference between closed and open shell molecules is less well described in density functional theory methods, as a result of the difference in electron correlation in closed vs. open shell system.¹⁵ Isodesmic reactions are implemented to cancel calculation error and achieve greater accuracy for the gas phase enthalpies of formation. These reactions are hypothetical reactions which incorporate similar bonding environments for both reactants and products that allows for cancellation of error associated with each method of analysis. Isodesmic reactions conserve the number and type of bonds on both sides of an equation. In the equation, two products and one reactant are reference molecules for which the thermodynamic properties known.

$$\Delta_{\text{rxn}}H^{\circ}_{298} = \sum \Delta H_f \text{ products} - \sum \Delta H_f \text{ reactants}$$

The calculated enthalpy of each species in the hypo-theoretical work reaction is used to calculate the enthalpy of reaction, $\Delta_{\text{rxn}}H^{\circ}_{298}$. Literature values for enthalpies of formation of the three reference compounds are then used along with the calculated $\Delta_{\text{rxn}}H^{\circ}_{298}$ to obtain the enthalpies of formation on the target molecules.¹⁶ Standard enthalpies of formation at 298.15 K of the reference species used in the reactions are shown in Table 3.1.

Table 3.1 Standard Enthalpies of Formation at 298.15 K of References Species

Species	$\Delta_{\text{f}}H^{\circ}_{298}$ (kcal/mol)	Source (Ref. No.)
CH ₃ CH ₃	-20.04	21
CH ₃ CH ₂ CH ₃	-25.02	21
CH ₃ CHO	-39.6 ± 0.1	7
CH ₃ CH ₂ CHO	-45.09 ± 0.18	22
CH ₂ =CHCH ₃	4.879	21
CH ₂ =CHCH ₂ CH ₃	-0.15 ± 0.19	21
CH ₃ CH=CHCH ₃ (trans)	-1.5 ± 0.30	7
CH ₃ CH=CHCH ₃ (cis)	-2.7 ± 0.2	7
CH ₃ C(=O)CH ₃	-51.90 ± 0.12	21
CH ₂ =CH ₂	12.54	21
C ₆ H ₆	19.8 ± 0.2	21
CH ₂ =CH·	71.2 ± 0.2	7
C·H=CHCH ₃	63.66	23
CH ₂ =CHCH=CH ₂	26.5 ± 0.9	21
CH ₂ =C·CH=CH ₂ ^a	75	24
CH ₂ =CHCH=C·H	85.4	25
CH ₂ =C·CH ₃	58.6	21
CH ₂ ·CHO	4.4 ± 0.9	7
CH ₃ C·HCHO ^b	-5.7 ± 0.9	7
CH ₃ C·O	-2.3 ± 0.1	7
CH ₃ CH ₂ C·O	-6.9 ± 0.9	7
CH ₃ CH ₂ C(=O)CH ₃	-57.02 ± 0.20	21
CH ₃ C·HC(=O)CH ₃	-18.6 ± 0.4	19
C·H=CHCH ₂ CH ₃	59.3 ± 0.9	7
C·H=CHCHO	44.4 ± 0.9	7

a. Resonant forms are CH₂=C·-C(-H)=CH₂ & CH₂=C=C(-H)-C·H₂

b. Resonant forms are CH₃-C·H-CHO & CH₃-CH=CH(-O·)

Each of the parent compounds is analyzed with five isodesmic work reactions. Each parent species contains one carbon – carbon double bond (olefin) group and an aldehyde carbonyl group. The species used in the work reactions for these parent species all incorporate an olefin and a carbonyl group in order to obtain error cancelation for the corresponding bonding of these groups. The agreement obtained between the different work reactions and the different species in the reactions lends support to accuracy of the calculation values. There is also very good agreement between the computational methods. The work reactions for the parent stable species are listed in Table 3.2.

Table 3.2 Isodesmic Reactions and Calculated $\Delta_f H^\circ_{298}$ at 298 K for Target Molecules

Work Reactions	Reaction Enthalpies (298 K) kcal/mol			$\Delta_f H^\circ_{298}$ kcal/mol		
	B3LYP/ 6-31g(d,p)	CBS-QB3	M062X/ 6-31+G(d,p)	B3LYP/ 6-31g(d,p)	CBS-QB3	M062X/ 6-31+G(d,p)
cdccdo(ch2chcho)						
cdccdo + cc → ccdo + cdcc	3.71	2.38	0.95	-18.67	-17.34	-15.91
cdccdo + ccc → ccdo + cdcc(cis)	0.74	0.10	-0.50	-17.15	-16.18	-15.58
cdccdo + ccc → ccdo + cdcc(trans)	-1.18	-1.32	-1.73	-16.10	-15.96	-15.55
cdccdo + ccc → ccdo + cdccc	2.63	1.52	1.22	-17.36	-16.25	-15.95
cdccdo + ccc → cccdo + cdcc	4.29	3.05	1.62	-19.76	-18.52	-17.09
Average				-17.81	-16.85	-16.02
Standard Deviation				1.27	0.96	0.56
cdcccdo(ch2chch2cho)						
cdcccdo + cc → cccdo + cdcc	1.24	0.85	-0.47	-21.69	-21.30	-19.98
cdcccdo + cc → ccdoc + cdcc	-6.79	-6.90	-8.89	-20.47	-20.36	-18.37
cdcccdo + cc → ccdo + cdccc	-0.42	-0.68	-0.87	-19.29	-19.03	-18.84
cdcccdo + c6h6 → y(c6h5)cdo + cdcc	-5.89	-4.50	-5.76	-18.21	-19.62	-18.36
cdcccdo + cdc → cdcccdo + cdcc	-5.48	-3.65	-5.31	-20.27	-21.99	-18.65
Average				-20.43	-20.46	-18.84
Standard Deviation				1.25	1.08	0.60
cdcccdo(ch3chch2cho) trans						
cdcccdo + cc → cccdo + cdccc	3.26	2.86	2.39	-28.46	-28.06	-27.59
cdcccdo + cc → ccdo + cdcccc	2.67	1.82	1.55	-27.80	-26.95	-26.68
cdcccdo + cc → ccdoc + cdccc	-4.76	-4.89	-6.03	-27.25	-27.12	-25.98
cdcccdo + cc → cccdo + cdcc(cis)	1.38	1.45	0.67	-27.93	-28.00	-27.22
cdcccdo + cc → cccdo + cdcc(trans)	-0.54	0.02	-0.57	-27.21	-27.77	-27.18
Average				-27.73	-27.58	-26.93
Standard Deviation				0.46	0.46	0.55
cdcccdo(ch3chch2cho) cis						
cdcccdo + cc → cccdo + cdccc	2.52	1.46	1.74	-27.72	-26.66	-26.94
cdcccdo + cc → ccdo + cdcccc	1.93	0.42	0.90	-27.06	-25.55	-26.03
cdcccdo + cc → ccdoc + cdccc	-5.51	-6.28	-6.67	-26.50	-25.72	-25.34
cdcccdo + cc → cccdo + cdcc(cis)	0.64	0.05	0.02	-27.19	-26.60	-26.57
cdcccdo + cc → cccdo + cdcc(trans)	-1.28	1.37	-1.22	-26.47	-26.38	-26.53
Average				-26.99	-26.18	-26.28
Standard Deviation				0.47	0.46	0.55
$\Delta_f H^\circ_{298}(\text{cis}) - \Delta_f H^\circ_{298}(\text{trans})^a$			$\Delta_{\text{cis-trn}}$	0.74	1.40	0.65
ΔH_{rxn} for Cis = Trans				0.74	1.39	0.64

Values are standard deviation of calculated values. They do not represent error limits. Error limits are larger a. from calculated enthalpies of reaction above.

The work reactions for the radical species are also chosen to have similar olefin, carbonyl and radical sites on both sides of the equations for error cancelation. These also include the parent specie to the radical on the product side of the target reacting molecule.

The calculated ΔH_{rxn} , the work reactions and the calculated enthalpies of formation of the target compounds are listed in Table 3.2. The average values in bold from CBS-QB3 are recommended. $\Delta_f H^\circ_{298}$ for parent molecules are, cdccdo ($\text{CH}_2=\text{CHCH}=\text{O}$), -16.85 kcal/mol, cdccdo trans ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}=\text{O}$), -27.58 kcal/mol, cdccdo cis ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}=\text{O}$), -26.18 kcal/mol, cdccdo ($\text{CH}_2=\text{CHCH}_2\text{CH}=\text{O}$), -20.46 kcal/mol. The trans conformation of $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}=\text{O}$ is more stable than cis form by 0.74 kcal/mol in B3LYP/6-31g(d,p) level, 1.39 kcal/mol in CBS-QB3 level, and 0.64 kcal/mol in M062X/6-31+G(d,p) level.

The different calculation method work reaction from CBS-QB3 show the lowest standard deviations and the CBS-QB3 method values are chosen as recommended. The minimum standard deviation for parent molecules is 0.46 kcal/mol, and the maximum standard deviation for parent molecules is 1.07 kcal/mol. The enthalpy of formation in CBS-QB3 level of cdccdo is in good agreement to the one calculated by Asatryan, da Silva and Bozzelli.⁴ The value from this study is -16.85 kcal/mol; the value from literature⁴ is -16.5 kcal/mol. The comparison is listed in Table 3.7. It is noted that these are standard deviations from the work reaction sets as a function of calculation method, they do not include error from the uncertainty of the reference specie in the reaction sets and they are not error limits.

The enthalpies of formation of radicals are listed in Table 3.3. The data demonstrates good agreement for the $\Delta_f H^\circ_{298}$ values between the B3LYP/6-31g(d,p),

CBS-QB3 and M062X/6-31+G(d,p). Because CBS-QB3, is the highest level method in this study and has the lowest standard deviation; the values in bold from CBS-QB3 are recommended. $\Delta_f H^\circ_{298}$ for radicals are, **cjdccdo**, 42.91 kcal/mol, **cdcjcd**, 43.87 kcal/mol, **cdccjdo**, 21.53 kcal/mol, **cjdcccd**, 7.49 kcal/mol, **ccjdcccd**, 28.50 kcal/mol, **cdccjcd**, 29.90 kcal/mol, **cdccjcd**, -1.83 kcal/mol, **cdcccjdo**, 9.38 kcal/mol, **cjdcccd**, 38.74 kcal/mol, **cdccjcd**, 35.83 kcal/mol, **cdccjcd**, 5.93 kcal/mol, and **cdcccjdo**, 16.78 kcal/mol. In CBS-QB3 method, the minimum standard deviation of radicals is 0.07 kcal/mol, and the maximum standard deviation is 0.80 kcal/mol.

Table 3.3 Isodesmic Work Reactions and Calculated Enthalpies of Formation at 298 K of Radicals

Work Reactions	Reaction Enthalpies (298K) kcal/mol			$\Delta_f H^\circ(298)$ kcal/mol		
	B3LYP/ 6-31g(d,p)	CBS-QB3	M062X/ 6-31G(d,p)	B3LYP/ 6-31g(d,p)	CBS-QB3	M062X/ 6-31+G(d,p)
cdecco system						
cjdccdo						
cjdccdo+cdc \rightarrow cdecco+cdej	-1.21	-1.18	-1.18	42.06	42.99	43.82
cjdccdo+cdec \rightarrow cdecco+cjdcc	-0.63	-0.71	-0.37	41.88	42.92	43.81
cjdccdo+cdecc \rightarrow cdecco+cjdecc	-0.22	-0.21	-0.16	41.86	42.81	43.59
Average				41.93	42.91	43.61
Standard Deviation				0.09	0.07	0.17
Bond Energy				111.84	111.86	111.73
cdcejdo						
cdcejdo+cdec \rightarrow cdecco+cdejc	-6.35	-6.12	-5.27	42.54	43.27	43.25
cdcejdo+cdecde \rightarrow cdecd + cdcecj	-13.43	-11.99	-12.30	44.12	43.64	44.78
cdcejdo+cdecde \rightarrow cdecco + cdcecj	0.46	-0.89	-0.60	40.63	42.94	43.48
cdcejdo+ccdo \rightarrow cdecco+cjdo	-17.67	-17.15	-17.58	43.86	44.30	45.57
cdcejdo+cccdo \rightarrow cdecco+cejdo	-24.66	-22.65	-23.78	46.24	45.19	47.15
Average				43.38	43.87	44.85
Standard Deviation				1.86	0.80	1.43
Bond Energy				113.39	112.82	112.96
cdcejdo						
cdcejdo+ccdo \rightarrow cdecco+cejdo	0.71	-0.85	-0.85	18.78	21.30	22.13
cdcejdo+cccdo \rightarrow cdecco+cccjdo	0.17	-1.15	-1.45	20.21	22.49	23.63
cdcejdo+cccdoc \rightarrow cdecco+cejdoc	0.04	0.77	-0.11	20.57	20.80	22.51
Average				19.86	21.53	22.76
Standard Deviation				0.77	0.71	0.64
Bond Energy				89.77	90.48	90.87

Table 3.3 Isodesmic Work Reactions and Calculated Enthalpies of Formation at 298 K of Radicals (Continued)

cdcccd system						
cjdccdo						
cjdccdo +cdc→cdccdo+cdej	24.96	23.51	22.45	5.96	7.57	9.28
cjdccdo+cdcc→cdccdo+cjdc	25.54	23.98	23.27	5.79	7.50	8.87
cjdccdo+cdccc→cdccdo+cjdccc	25.96	24.48	23.47	5.76	7.39	9.05
Average				5.84	7.49	9.07
Standard Deviation				0.09	0.07	0.17
Bond Energy				85.67	87.17	88.09
ccjdccdo						
ccjdccdo +cdc→cdccdo+cdej	4.04	2.50	2.98	26.89	28.58	28.75
ccjdccdo +cdcc →cdccdo + cjdc	4.62	2.97	3.03	26.71	28.51	29.10
ccjdccdo+cdccc → cdccdo + cjdccc	5.03	3.47	4.00	26.69	28.40	28.52
Average				26.76	28.50	28.79
Standard Deviation				0.09	0.07	0.24
Bond Energy				106.59	108.18	107.82
ccdejccdo						
ccdejccdo +cdcc→cdccdo+cdejc	-2.85	-2.88	-1.53	29.11	29.30	28.60
ccdejccdo +cdccc→cdccdo+cdeccj	-9.92	-8.75	-8.56	30.69	29.67	30.13
ccdejccdo +cdccc→cdccdo+cdeccj	3.97	2.36	3.14	27.20	28.97	28.83
ccdejccdo+ccdo→cdccdo+cjedo	-14.16	-13.91	-13.84	30.43	30.33	30.92
ccdejccdo +ccdo →cdccdo +ccjedo	-21.16	-19.41	-20.04	32.81	31.22	32.50
Average				30.05	29.90	30.20
Standard Deviation				1.85	0.80	1.43
Bond Energy				109.88	109.58	109.22
ccdcjedo						
ccdcjedo +cdcc →cdccdo +cdejc	31.69	28.85	29.73	-5.42	-2.43	-2.66
ccdcjedo +cdccc →cdccdo+cdeccj	24.61	22.98	22.70	-3.84	-2.06	-1.13
ccdcjedo +cdccc →cdccdo+cdeccj	39.05	34.08	34.41	-7.88	-2.76	-2.43
ccdcjedo +ccdo→cdccdo+cjedo	20.37	17.82	17.42	-4.10	-1.40	-0.35
ccdcjedo +ccdo→cdccdo+ccjedo	13.38	12.32	11.22	-1.72	-0.51	1.24
Average				-4.59	-1.83	-1.07
Standard Deviation				2.02	0.80	1.43
Bond Energy				75.24	77.85	77.96
cdcccjdo						
cdcccjdo +ccdo→cdccdo+ccjdo	0.44	0.57	0.78	9.13	9.15	9.60
cdcccjdo +ccdo→cdccdo+cccjdo	-0.10	0.27	0.17	10.56	10.34	11.09
cdcccjdo +cccdo→cdccdo+ccjdoc	-0.23	2.19	1.52	10.92	8.65	9.97
Average				10.20	9.38	10.22
Standard Deviation				0.77	0.71	0.63
Bond Energy				90.03	89.06	89.25

Table 3.3 Isodesmic Work Reactions and Calculated Enthalpies of Formation at 298 K of Radicals (Continued)

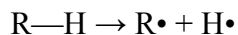
cdccdo system						
ejdccdo						
ejdccdo +cdc→cdccdo+cjdc	-0.60	-0.66	-0.69	38.83	38.86	40.51
ejdccdo+cdccdo→cdccdo+ejdccdo	0.61	0.52	0.49	38.70	38.78	40.30
ejdccdo+cdcc→cdccdo+ejdcc	-0.03	-0.19	0.12	38.65	38.79	40.10
ejdccdo+cdcc→cdccdo+cdccjc	-5.99	-4.96	-3.69	39.28	38.50	38.85
Average				38.87	38.74	39.94
Standard Deviation				0.25	0.14	0.65
Bond Energy				111.40	111.29	110.88
cdccjdo						
cdccjdo+cdc→cdccdo+cjdc	3.37	2.25	2.24	34.86	35.96	37.58
cdccjdo+cdccdo→cdccdo+ejdccdo	4.58	3.43	3.42	34.73	35.87	37.37
cdccjdo+cdcc→cdccdo+ejdcc	3.95	2.72	3.05	34.68	35.88	37.17
cdccjdo+cdcc→cdccdo+cdccjc	-2.02	-2.06	-0.76	35.59	35.60	35.92
Average				34.97	35.83	37.01
Standard Deviation				0.37	0.14	2.14
Bond Energy				107.50	108.39	107.95
cdccjdo						
cdccjdo +cdc→cdccdo+cjdc	35.13	32.14	30.99	3.10	6.06	8.83
cdccjdo+cdccdo→cdccdo+ejdccdo	36.34	33.33	32.17	2.98	5.97	8.62
cdccjdo+cdcc→cdccdo+ejdcc	35.70	32.62	31.80	2.92	5.98	8.42
cdccjdo+cdcc→cdccdo+cdccjc	29.74	27.84	27.99	3.83	5.70	7.17
Average				3.21	5.93	8.26
Standard Deviation				0.36	0.14	0.65
Bond Energy				75.74	78.49	79.20
cdcccjdo						
cdcccjdo+cdc→cdccdo+cjdc	21.53	21.29	20.74	16.70	16.91	19.08
cdcccjdo+cdccdo→cdccdo+ejdccdo	22.74	22.47	21.93	16.57	16.83	18.86
cdcccjdo+cdcc→cdccdo+ejdcc	22.11	21.76	21.56	16.52	16.84	18.66
cdcccjdo+cdcc→cdccdo+cdccjc	16.14	16.99	17.75	17.43	16.55	17.42
Average				16.80	16.78	18.50
Standard Deviation				0.37	0.14	0.64
Bond Energy				89.34	89.34	89.44

The enthalpy of formation in CBS-QB3 level determination for cdccjdo are in good agreement to the ones calculated by Rutz, da Silva and Bozzelli.⁵ The value from this study is 21.53 kcal/mol; the value from literature⁵ is 21.9 kcal/mol. Comparisons for thermochemical properties from this study and report by Rutz, da Silva and Bozzelli are list in Table 3.8.

Compared the enthalpy of formation of 2-propenal and corresponding radicals calculated by Goldsmith, Magoon and Green, values calculated in M062X/6-31+G(d,p) level show agreement with the Goldsmith et al method⁷ where atomization method was used. The enthalpy of formation for cdccdo from this study is -16.02 kcal/mol at M062X/6-31+G(d,p) level and -16.85 kcal/mol at CBS-QB3 level, the value from literature⁷ is -15.5 kcal/mol; for cjddcdo, value from this study is 43.61 kcal/mol in M062X/6-31+G(d,p) level and 42.91 kcal/mol in CBS-QB3 level, the value from literature⁷ is 44.4 kcal/mol; for cdcjcd, value from this study is 44.85 kcal/mol in M062X/6-31+G(d,p) level and 43.87 kcal/mol in CBS-QB3 level, the value from literature⁷ is 45.2 kcal/mol; for cdccjdo, value from this study is 22.76 kcal/mol in M062X/6-31+G(d,p) level and 21.53 kcal/mol in CBS-QB3 level, the value from Goldsmith literature⁷ is 23.2 kcal/mol. Comparisons for thermochemical properties from this study and by Goldsmith, Magoon and Green are listed in Table 3.9.

3.3 Bond Enthalpies

The calculated $\Delta_f H^\circ_{298}$ of the parent and of the radical species corresponding to loss of a hydrogen atom are used along with standard enthalpy of formation of 52.1 kcal/mol for the hydrogen atom.¹⁶ A bond cleavage reaction is used to calculate bond enthalpy.



Parent molecules bond enthalpies are computed from work reactions listed in Table 3.4 and corresponding data for radical is listed in Table 3.3. C-H bond enthalpies from CBS-QB3 and M062X/6-31+G(d,p) levels show excellent agreement.

Analysis of the C-H bond of enthalpies for the unsaturated carbonyl in this study can be broken down into six bond types: (i) primary adjacent to vinyl, (ii) secondary adjacent to the carbonyl, (iii) primary vinyl, (iv) secondary vinyl, (v) secondary vinyl adjacent to carbonyl, (vi) carbonyl. Table 3.4 has a summary of these different bond classes for unsaturated carbonyl parent molecules.

Table 3.4 Summary of C-H Bond Enthalpies from This Study

Species	Carbon- Hydrogen Bond Dissociation Classes (kcal/mol)					
	Primary adjacent to vinyl	Secondary Adjacent to Carbonyl	Primary Vinyl	Secondary Vinyl	Secondary Vinyl Adjacent to Carbonyl	Carbonyl
cdccdo			111.8		113.1	90.4
cdcccd	87.0	77.0 s + allylic		107.5,109.6		89.4
cdccdo		77.81s + allylic	111.2	108.0		89.4
References	88		110-112	102-111		87-89

Available Literature Value, Ref^{17, 18, 19}

The primary C-H bond adjacent to vinyl of $C(-H)C=CCC=O$ has bond enthalpy 87.0 kcal/mol, which is lower than the literature value, published by Luo¹⁷, by approximately 1 kcal/mol. The primary C-H bond enthalpy is 87 kcal/mol. There is a 14 kcal/mol stabilization from resonance, compared to 101 kcal/mol primary C-H bond enthalpy, because the odd carbon electron conjugate to vinyl pi bond.

The values for the secondary C-H bond enthalpies, adjacent to carbonyl group, are: 77.0 kcal/mol for $CC=CC(-H)C=O$ and 77.8 kcal/mol for $C=CC(-H)C=O$. Comparing this to a secondary C-H bond enthalpy (98.5 kcal/mol) for a normal alkane and 94.5 for a normal secondary adjacent to a ketone by Hudzik and Bozzelli.¹⁰ The high stabilization in allylic secondary C-H bond is due to resonance between the carbonyl group and secondary carbon.

The primary vinyl C-H bond enthalpies for $C(-H)=CC=O$ and $C(-H)=CCC=O$ are 111.8 kcal/mol and 111.2 kcal/mol, which are similar to 110-112 kcal/mol from literature values.¹⁷ The secondary vinyl C-H bond enthalpies for $CC(-H)=CCC=O$, $CC=C(-H)CC=O$ and $C=C(-H)CC=O$ are 107.5 kcal/mol, 109.6 kcal/mol and 108.0 kcal/mol respectively. Compared to literature value, the secondary vinyl C-H bond enthalpies for $CC=CCC=O$ and $C=CCC=O$ are in the range of 102-111 kcal/mol for the bond enthalpies from the literature value in Moussaoui and Mare's report.¹⁹

The enthalpy for C-H bond at the position of secondary vinyl, adjacent to carbonyl group, $C=C(-H)C=O$ shows a very different trend; it is increased by ~ 5 kcal/mol to 113.1 kcal/mol from a conventional secondary vinyl on an olefin, which we evaluate as being ~ 108 kcal/mol. The carbonyl group is interpreted as drawing electrons from the vinyl group here. This increases the positive energy on the vinyl carbons which increase the C-H bond

energy. The C-H bond enthalpy of the primary vinyl of cdccdo is increased but only by 0.7 kcal/mol from a normal primary, which we evaluate as being ~ 111 kcal/mol.

The carbonyl C-H bond enthalpies for $C=CC=O$, $CC=CCC=O$ and $C=CCC=O$ are 90.4 kcal/mol, 89.4 kcal/mol and 89.4 kcal/mol. There is a reported range of 87-89 kcal/mol for C-H bond of enthalpies on aldehyde carbonyl group.¹³ The C-H bond enthalpy of aldehyde carbonyl in this study is the same as the carbonyl C-H bond strength in formaldehyde (87 ± 1 kcal/mol) indicating no extra stabilization energy as a result of the allylic group. The fact that different α substituents ($CH_2=CH$, $CH_2=CHCH_2$, $CH_3CH=CHCH_2$) in aldehydes appears to have a small effect on the carbonyl C-H bond strength decreasing of about 2 kcal/mol.

3.4 Entropy and Heat Capacity

The entropy S° and heat capacity $C_p(T)$ data for the parent molecules as a function of temperature are determined from the optimized structures, moments of inertia, vibrational frequencies, symmetries, electron degeneracy, mass of the molecules, number of optical isomers and internal rotor contributions.²⁰

Contributions of translation, vibration and external rotation to entropy and heat capacity for each parent molecule and radical are calculated using the SMCPS program with rigid-rotor-harmonic-oscillator approximation for vibration frequencies and vibration frequencies adjusted as recommended by Scott and Radom.¹⁴ The SMCPS program utilizes the rigid-harmonic oscillator approximation from the optimized structures obtained at B3LYP/6-31G (d,p) level.

Internal rotor torsion frequencies are identified using visual inspection of the torsion frequency movement in GaussView and calculated rotor contributions are used to

replace the vibration torsion contribution. The lower frequency is selected, in case when identification of a frequency is uncertain due to coupling to other motions. As noted the torsion frequencies contributions are replaced with entropy and heat capacity contributions from “VIBIR” program for hindered rotor analysis. In this study, internal rotor barriers with energy below 6.5 kcal/mol are treated; internal rotors with barriers higher than 6.5 kcal/mol are calculated as the torsion frequency contributions. Table 3.5 has a summary of the internal rotor torsion frequencies identified using GaussView.

Table 3.5 Internal Rotor Torsion Frequencies, not Listed in SMCPS Input Files

species	Internal rotor torsion frequencies (cm⁻¹)		
cdccdo	cdc--cdo 172.78		
cjdccdo	cjdc--cdo 165.99		
cdcccdo	c--cdcccdo 206.06	ccdc--ccdo 65.75	ccdcc--cdo 137.70
cjdcccdo	cjdc--ccdo 73.56	cjedcc--cdo 58.01	
ccjdcccdo	c--cjcccdo 129.46	ccjdc--ccdo 54.63	ccjdcc--cdo 139.68
cdcejccdo	c--cdcejccdo 190.36	ccdcj--ccdo 78.95	cdcejc--cdo 48.58
cdcejjcdo	c--cdcejjcdo 155.36	ccdc--cjjcdo 255.03	
cdcccjdo	c--cdcccjdo 205.88	ccdc--ccjdo 130.24	ccdcc--cjdo 60.22
cdccdo	cdc--ccdo 74.14	cdcc--cdo 156.43	
cjdccdo	cjdc--ccdo 74.24	cjdcc--cdo 156.36	
cdcejcdo	cdcj--ccdo 164.03	cdcejc--cdo 136.48	
cdccjdo	cdc--cjdo 273.94		
cdcccjdo	cdc--ccjdo 142.86	cdcc--cjdo 73.58	

Heat capacities and entropies for parent unsaturated carbonyl alkenes and corresponding radicals from SMCPS and VIBIR are listed in Table 3.6 and Table B.2. Comparisons for thermochemical properties from this study and literatures are listed in Table 3.7-3.9. The tables show great agreement between values from this study and from literatures.

Table 3.6 Comparison of Heat Capacities for Parent Species from SMCPS and VIBIR.

Species	Cp(T) (cal/mol/K)							Method	Rotors
	300k	400k	500k	600k	800k	1000k	1500k		
T									
cdccdo	15.74	19.35	22.55	25.26	29.50	32.58	37.28	SMCPS	0
	15.90	19.53	22.78	25.55	29.85	32.91	37.33	SMCPS+VIBIR	1
cjdccdo	15.80	18.95	21.55	23.70	26.99	29.35	32.92	SMCPS	0
	15.98	19.18	21.85	24.05	27.34	29.60	32.79	SMCPS+VIBIR	1
cdcejdo	16.16	19.00	21.48	23.59	26.90	29.31	32.94	SMCPS	0
cdccjdo	16.87	19.87	22.24	24.16	27.12	29.32	32.78	SMCPS	0
cdcccdo (trans)	26.24	32.88	38.88	44.01	52.15	58.11	67.18	SMCPS	0
	26.00	31.85	37.31	42.11	49.82	55.55	64.40	SMCPS+VIBIR	3
cdcccdo (cis)	26.11	32.84	38.87	44.04	52.15	58.09	67.15	SMCPS	0
	25.58	31.96	37.78	42.80	50.60	56.26	64.86	SMCPS+VIBIR	3
cejdeccdo	25.73	32.26	37.86	42.53	49.68	54.81	62.71	SMCPS	0
	25.89	31.91	37.12	41.50	48.29	53.26	60.91	SMCPS+VIBIR	2
cejdeccdo	26.21	32.21	37.57	42.18	49.42	54.73	62.76	SMCPS	0
	25.58	30.78	35.69	39.99	46.91	52.05	59.92	SMCPS+VIBIR	3
cdcejccdo	26.16	32.15	37.52	42.12	49.35	54.64	62.68	SMCPS	0
	25.58	30.83	35.72	40.02	46.90	52.01	59.86	SMCPS+VIBIR	3
cdcccejdo	25.56	31.79	37.33	42.05	49.35	54.64	62.64	SMCPS	0
	23.65	31.55	36.91	41.52	48.74	54.04	62.07	SMCPS+VIBIR	2
cdcccjdo	25.99	32.05	37.43	42.02	49.20	54.46	62.51	SMCPS	0
	25.87	31.13	35.95	40.17	46.91	51.94	59.75	SMCPS+VIBIR	3
cdcccdo	20.87	26.16	30.82	34.77	40.93	45.42	52.26	SMCPS	0
	19.81	24.78	29.26	33.10	39.12	43.55	50.33	SMCPS+VIBIR	2
cjdcccdo	20.95	25.75	29.82	33.20	38.41	42.18	47.90	SMCPS	0
	20.66	24.90	28.62	31.79	36.76	40.42	46.01	SMCPS+VIBIR	2
cdcejccdo	21.06	25.71	29.70	33.07	38.31	42.12	47.89	SMCPS	0
	20.28	24.47	28.22	31.45	36.53	40.27	45.97	SMCPS+VIBIR	2
cdccjdo	20.29	25.19	29.39	32.88	38.18	41.98	46.89	SMCPS	0
	18.57	25.38	29.57	33.06	38.41	42.28	48.10	SMCPS+VIBIR	1
cdcccjdo	20.60	25.30	29.35	32.74	37.97	41.77	47.59	SMCPS	0
	20.38	24.51	28.21	31.37	36.35	40.02	45.72	SMCPS+VIBIR	2

Table 3.7 Comparison of Thermochemical Properties of 2-Propenal from This Study and Literature Values by Asatryan, da Silva and Bozzelli⁴

T(K)	$\Delta_f H^\circ_{298}$ (kcal/mol)		Cp (cal/mol/K)		S ^o (cal/mol/K)	
	Ref 4	this study	this study SMCPS+VIBIR	Ref 4	this study SMCPS+VIBIR	Ref 4
298	-16.5	-16.85 ^a	21.9	16.47	66.72	68.17
300			15.90	16.55	68.70	66.82
400			19.53	20.28	73.59	72.11
500			22.78	23.51	78.07	76.99
600			25.55	26.19	82.29	81.52
800			29.85	30.26	89.97	89.64
1000			32.91	33.14	96.75	96.72
1500			37.33	37.35	110.63	111.07

a. Value calculated in CBS-QB3 method

Table 3.8 Comparison of Thermochemical Properties of Radical cdccjdo from This Study and Literature Values by Rutz, da Silva and Bozzelli⁵

T(K)	$\Delta_f H^\circ_{298}$ (kcal/mol)		Cp (cal/mol/K)		S ^o (cal/mol/K)	
	Ref 5	this study	Ref 5	this study SMCPS+VIBIR	Ref 5	this study SMCPS+VIBIR
298	21.9	21.53 ^a			67.98	68.17 ^a
300			15.53	16.87		
400			18.46	19.87		
500			21.03	22.24		
600			23.18	24.16		
800			26.50	27.12		
1000			28.92	29.32		
1500			32.62	32.78		

a. Value calculated in CBS-QB3 method

Table 3.9 Comparison of Thermochemical Properties of cdcdo and Corresponding Radicals from This Study and Reference Value by Goldsmith⁷

	cdcdo		cjdcdo		cdcjdo		cdccjdo	
	this study	Ref 7	this study	Ref 7	this study	Ref 7	this study	Ref 7
$\Delta_f H^\circ_{298}$	-16.02 ^a -16.85 ^b	-15.5	43.61 ^a 42.91 ^b	44.4	44.85 ^a 43.87 ^b	45.2	22.76 ^a 21.53 ^b	23.2
S°_{298}	68.70	65.3	70.01	67.3	70.00	70.3	68.17	67.9
T(K)	Cp (T)							
300	15.90	16.9	15.98	16.2	16.16	16.3	16.87	15.6
400	19.53	20.4	19.18	19.7	19.00	19.1	19.87	18.6
500	22.78	23.5	21.85	22.7	21.48	21.6	22.24	21.2
600	25.55	26.1	24.05	25.0	23.59	23.7	24.16	23.3
700	29.85	30.1	27.34	28.3	26.90	27.0	27.12	26.6
1000	32.91	33.0	29.60	30.4	29.31	29.4	29.32	29.1
1500	37.33	37.3	32.79	33.2	32.94	33.0	32.78	32.7

Units of $\Delta_f H^\circ_{298}$ in kcal/mol

Units of Cp(T) and S°_{298} in cal/mol/K

a. Value calculated in M062X/6-31+G(d,p) method

b. Value calculated in CBS-QB3 method

CHAPTER 4

SUMMARY

Thermochemical properties, including enthalpies of formation, entropy, heat capacity, and bond enthalpies are determined for the C3 to C5 unsaturated carbonyl alkenes and corresponding radicals. The enthalpies of formation of the target molecules, averaged over five isodesmic reactions for molecule $C=CC=O$, $CC=CCC=O$, and $C=CCC=O$ are evaluated as 16.89, 27.41 and 19.91 kcal/mol respectively. There is good consistency with the B3LYP method for the enthalpies of formation between the CBS-QB3 and M062X/6-31+G(d,p) levels of theory, with differences less than 0.71 kcal/mol for target molecules, and less than 1.73 kcal/mol for their corresponding radicals. The enthalpy of formation, entropy and heat capacity for 2-propenal and corresponding radicals are in satisfactory agreement with the limited literature data available. C-H Bond enthalpies of carbonyl in this study are in range of 89.4-90.4 kcal/mol, which are similar to carbonyl C-H bond strength in formaldehyde (87 ± 1 kcal/mol) indicating no extra stabilization energy as a result of the allelic group.

The bond enthalpy for the secondary C-H bonds, adjacent to carbonyl group, are quite low: 77.0 kcal/mol for $CC=CC(-H)C=O$ and 77.8 kcal/mol for $C=CC(-H)C=O$. The C--H bond enthalpy at the position of secondary vinyl, adjacent to carbonyl group, $C=C(-H)C=O$ shows a value of 113.1 kcal/mol, which is about 5 kcal/mol higher than a normal secondary vinyl C--H bond. The C-H bond enthalpy of the primary vinyl of $cdccdo$ is increased but only by 0.7 kcal/mol. These bond enthalpies are different from that normally found on olefins or carbonyls.

APPENDIX A

FIGURES

Figure A.1 to A.3 show potential barriers for parent molecules and radicals.

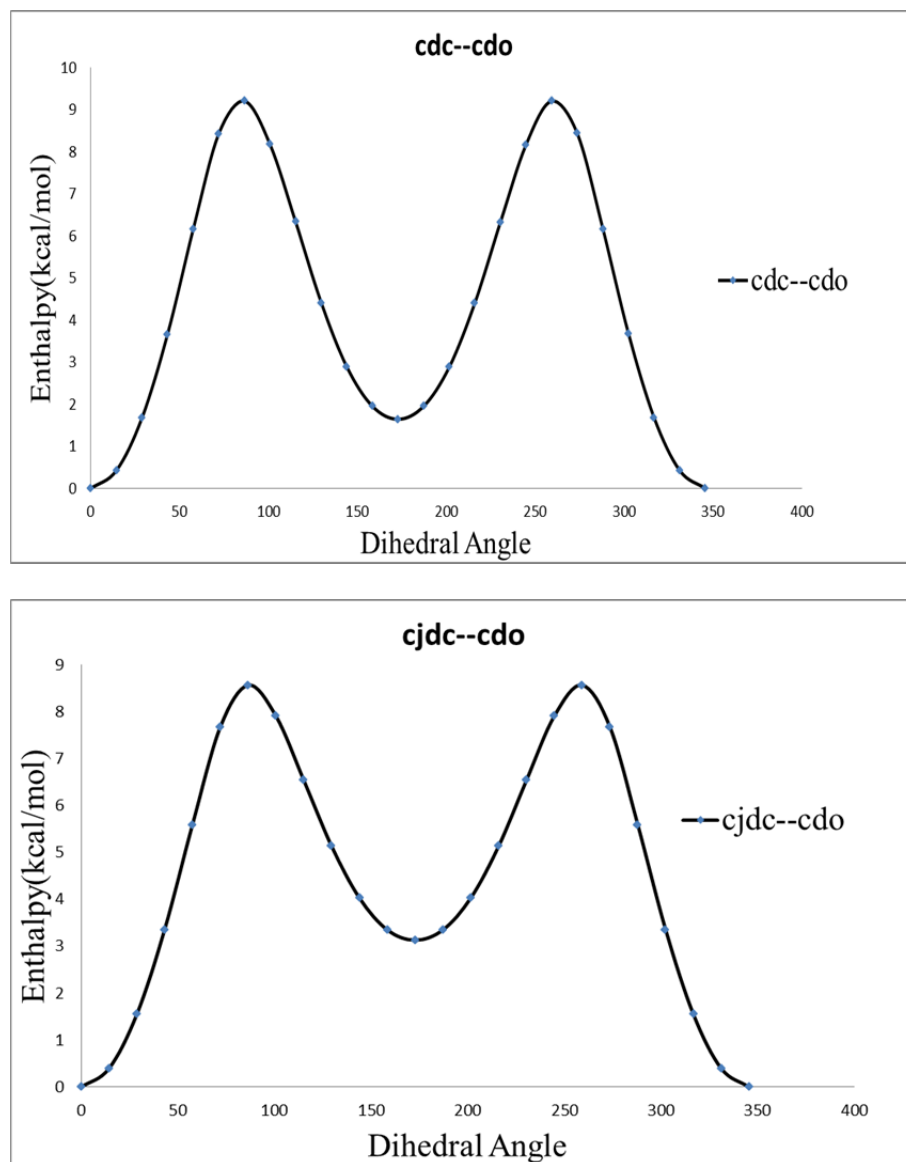


Figure A.1 Potential Energy Profiles for Internal Rotations in cdccdo and cjdcdo.

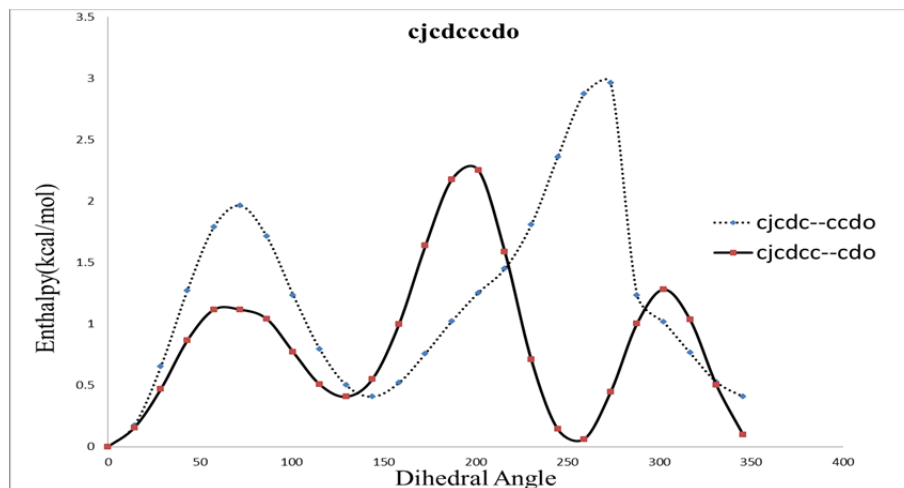
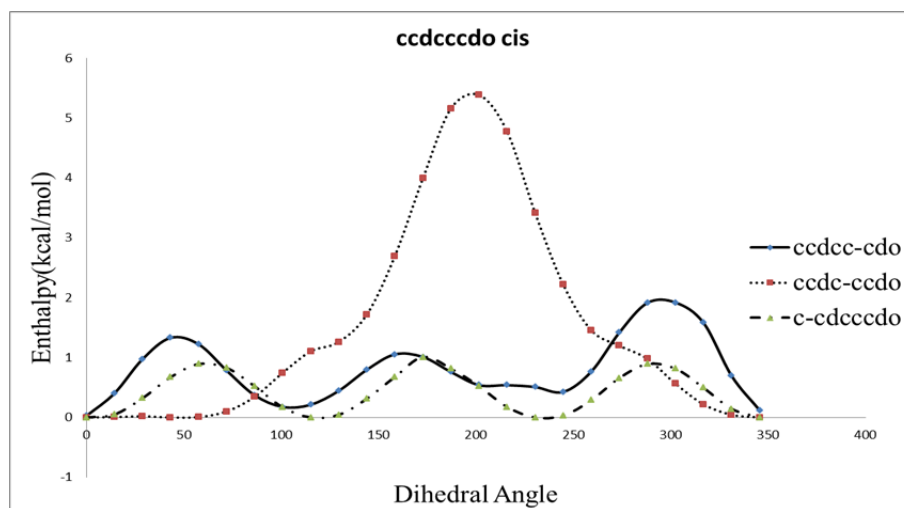
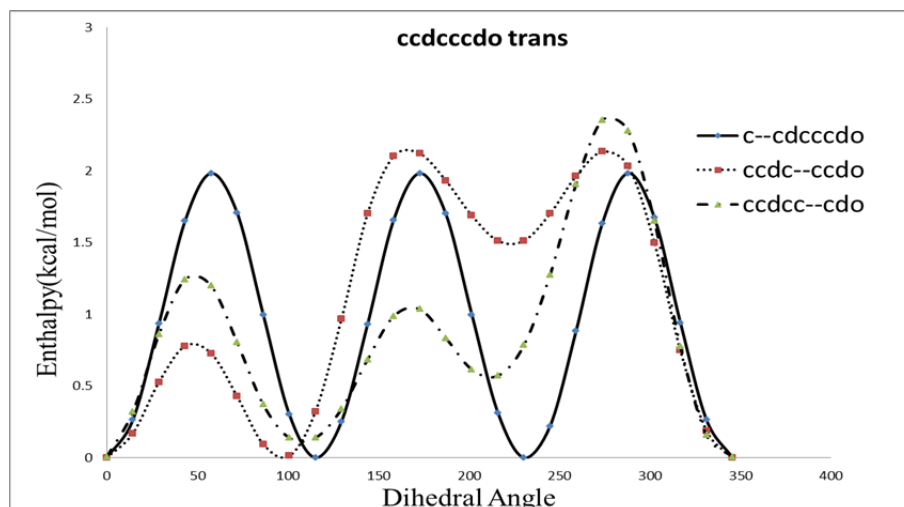


Figure A.2 Potential Energy Profiles for Internal Rotations in ccdccdo (trans), ccdcccdo (cis), cjdcccdo, cjdcccdo, cdcjccdo, cdccejcdo and cdcceccdo.

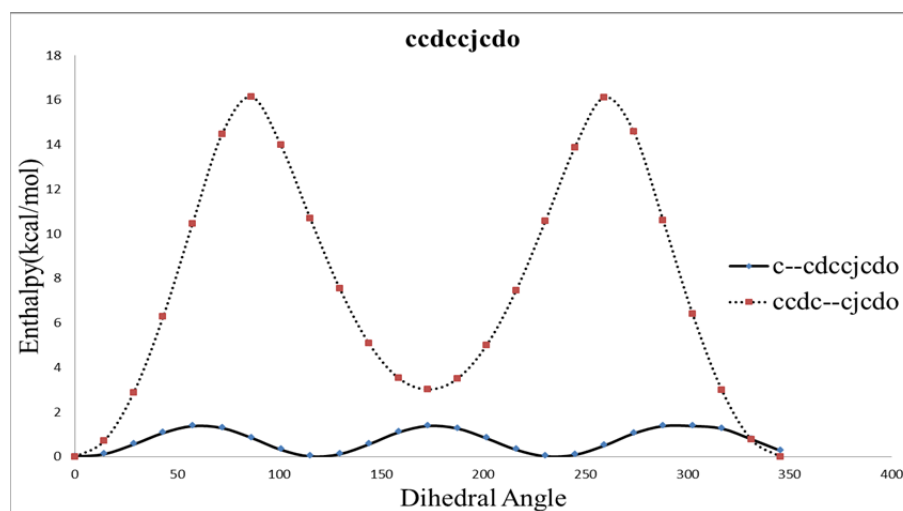
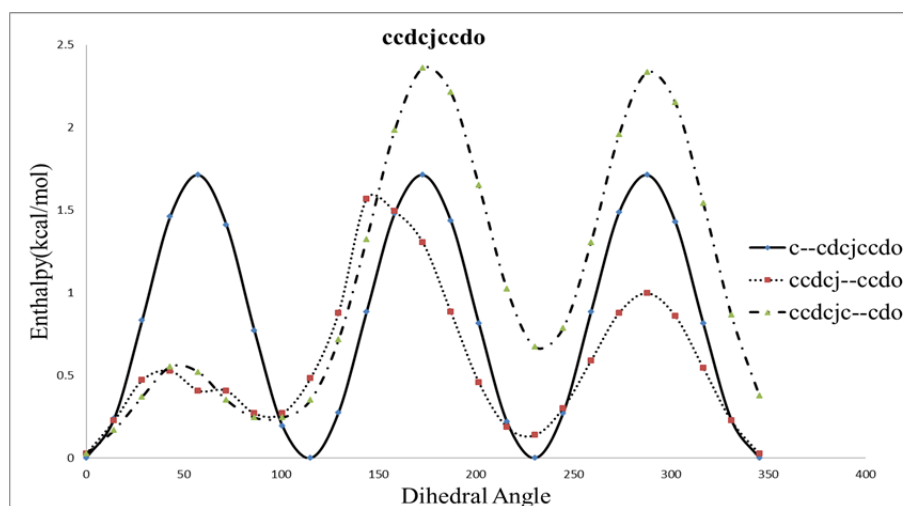
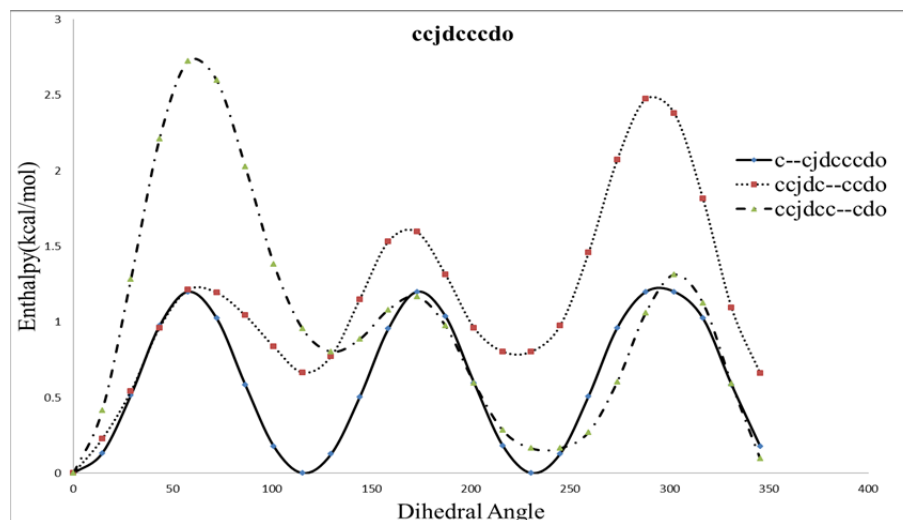


Figure A.2 Potential Energy Profiles for Internal Rotations in ccdeccdo (trans), ccdeccdo (cis), cjdccdo, ccjdccdo, ccdejcdo, ccdeccjdo and ccdeccjdo (Continued)

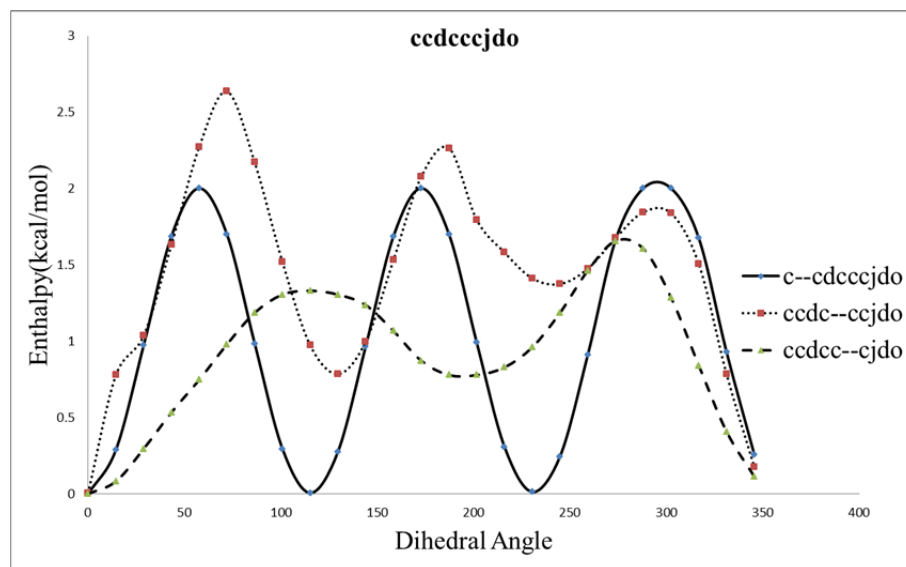


Figure A.2 Potential Energy Profiles for Internal Rotations in ccdcccdo (trans), ccdcccdo (cis), cjdcccdo, cejdcccdo, ccdcejdo, ccdccjdo and ccdcccdo. (Continued)

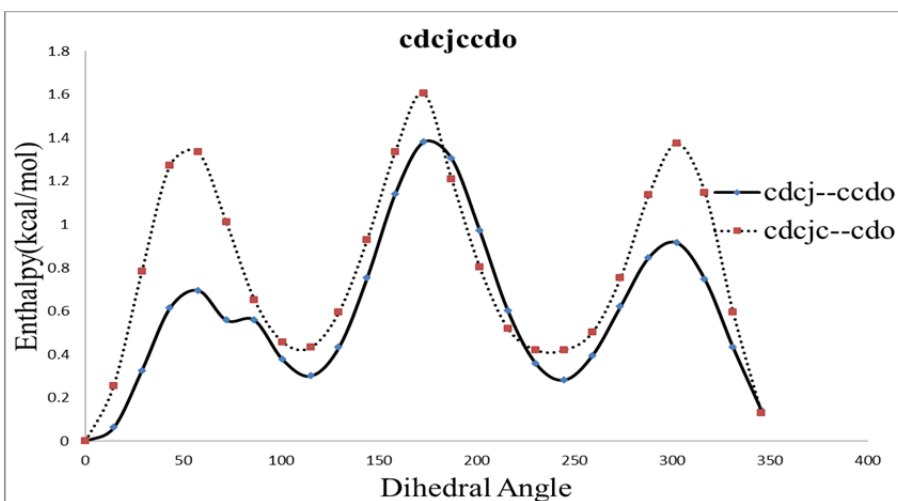
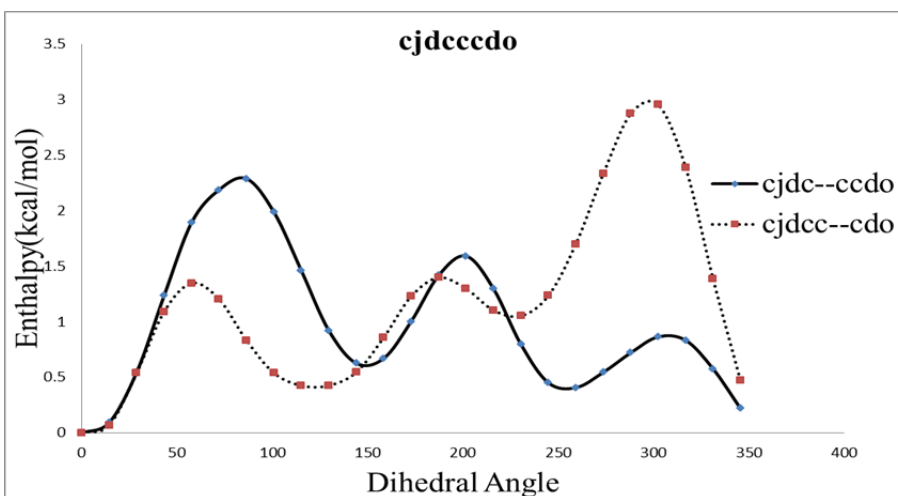
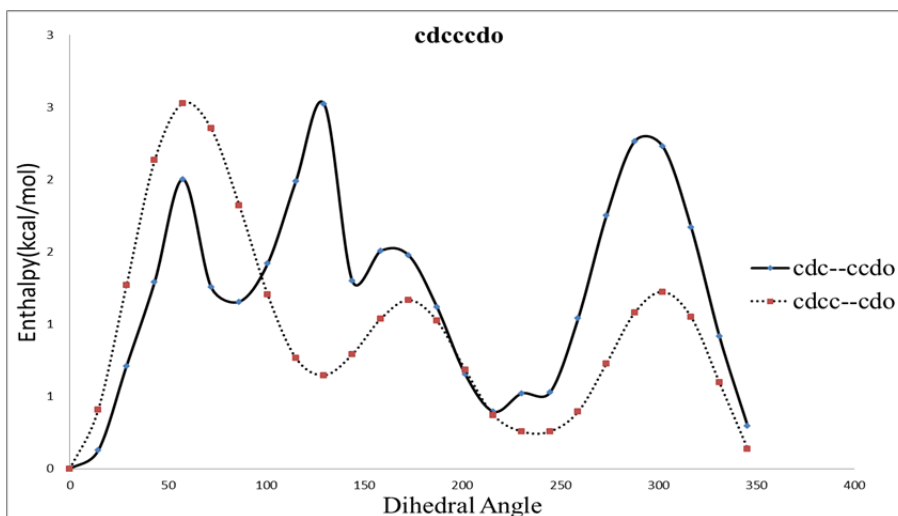


Figure A.3 Potential Energy Profiles for Internal Rotations in cdccedo, cjdccedo, cdcjccdo, cdccjedo and cdcccejdo.

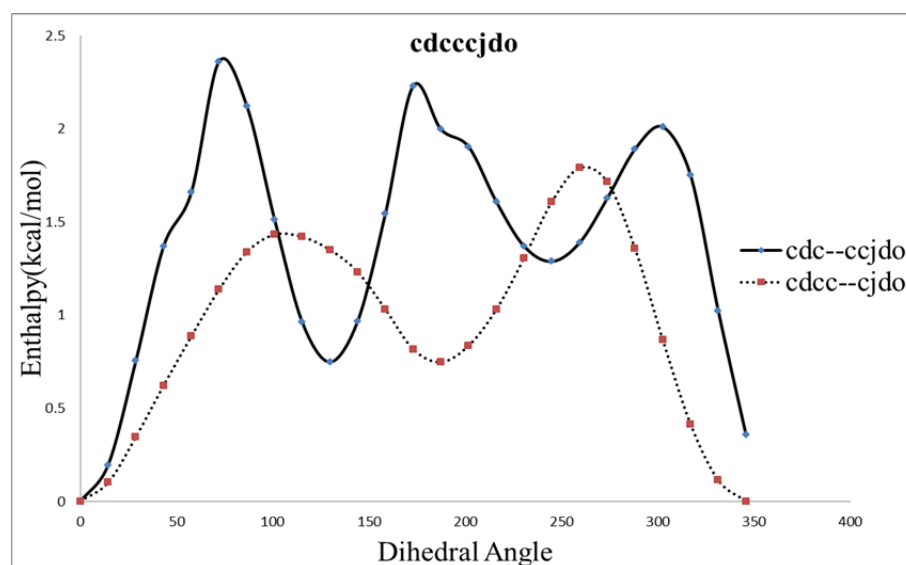
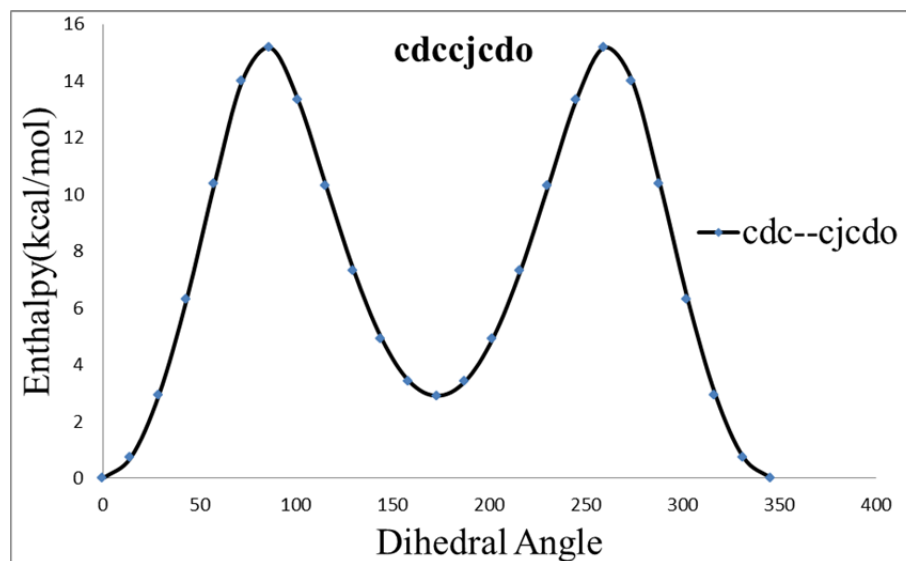


Figure A.3 Potential Energy Profiles for Internal Rotations in cdccdo, cjccdo, cdccjdo, cdcccjdo and cdcccjdo. (Continued)

APPENDIX B

PARAMETER RESULTS SUMMARY

Structure and thermo parameter results for parent molecules and radicals are provided in the following tables.

Table B.1 Optimized Structure Coordinates for Parent Molecules and Radicals from CBS-QB3 Level

Z-Matrix			
cdccdo	cjdcdo	cdcjcd	cdccjd
C	C	C	C
C,1,r21	C,1,r21	C,1,r21	C,1,r21
H,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
H,2,r42,1,a421,3,d4213,0	H,1,r41,2,a412,3,d4123,0	H,3,r43,2,a432,1,d4321,0	H,1,r41,2,a412,3,d4123,0
H,1,r51,2,a512,3,d5123,0	H,2,r52,3,a523,1,d5231,0	O,3,r53,2,a532,1,d5321,0	H,1,r51,2,a512,3,d5123,0
C,1,r61,2,a612,3,d6123,0	O,3,r63,2,a632,1,d6321,0	H,1,r61,2,a612,3,d6123,0	H,2,r62,1,a621,4,d6214,0
O,6,r76,1,a761,2,d7612,0	H,3,r73,2,a732,1,d7321,0	H,1,r71,2,a712,3,d7123,0	O,3,r73,2,a732,1,d7321,0
H,6,r86,1,a861,2,d8612,0	Variables:	Variables:	Variables:
Variables:	r21=1.31150413	r21=1.314873	r21=1.33346269
r21=1.33392472	r32=1.48700727	r32=1.47194469	r32=1.47592526
r32=1.08647744	r41=1.07932165	r43=1.10443891	r41=1.08366427
r42=1.08349908	r52=1.09401598	r53=1.21086884	r51=1.08442206
r51=1.0856196	r63=1.20698466	r61=1.08629531	r62=1.08953033
r61=1.47530358	r73=1.10796043	r71=1.09221286	r73=1.18510216
r76=1.20854383	a321=122.85674626	a321=133.94486599	a321=120.45532053
r86=1.11304943	a412=139.80699287	a432=116.57722257	a412=121.76298657
a321=120.95983101	a523=115.15068544	a532=121.91934908	a512=120.55947303
a421=122.29538112	a632=123.26845142	a612=122.32195804	a621=122.34960948
a512=122.42911211	a732=114.818632	a712=120.75787832	a732=128.32918951
a612=121.24024855	d4123=-179.99862705	d4321=-179.91353837	d4123=-179.99349392
a761=124.30405247	d5231=-179.99675056	d5321=0.09028959	d5123=-0.00246065
a861=114.47711313	d6321=-179.9998074	d6123=-179.98391735	d6214=0.00289567
d4213=179.99959195	d7321=-0.00162056	d7123=0.02203529	d7321=179.99958398
d5123=-179.9999018			
d6123=-0.00039659			
d7612=179.99052463			
d8612=0.01021259			

Table B.1 Optimized Structure Coordinates for Parent Molecules and Radicals from CBS-QB3 Level (Continued)

ccdccecd	cjcdcccd	ccjdcccd
<p>C</p> <p>C,1,r21</p> <p>C,2,r32,1,a321</p> <p>H,3,r43,2,a432,1,d4321,0</p> <p>C,3,r53,2,a532,1,d5321,0</p> <p>C,5,r65,3,a653,4,d6534,0</p> <p>O,6,r76,5,a765,3,d7653,0</p> <p>H,1,r81,2,a812,3,d8123,0</p> <p>H,1,r91,2,a912,8,d9128,0</p> <p>H,1,r101,2,a1012,8,d10128,0</p> <p>H,2,r112,1,a1121,8,d11218,0</p> <p>H,5,r125,3,a1253,2,d12532,0</p> <p>H,5,r135,3,a1353,12,d135312,0</p> <p>H,6,r146,5,a1465,7,d14657,0</p> <p>Variables:</p> <p>r21=1.50002563</p> <p>r32=1.33070234</p> <p>r43=1.08705514</p> <p>r53=1.49936269</p> <p>r65=1.51632858</p> <p>r76=1.20330105</p> <p>r81=1.09580836</p> <p>r91=1.09232193</p> <p>r101=1.0956047</p> <p>r112=1.09005649</p> <p>r125=1.10274312</p> <p>r135=1.09726327</p> <p>r146=1.1138317</p> <p>a321=125.15029716</p> <p>a432=119.60292112</p> <p>a532=124.55355076</p> <p>a653=114.75401626</p> <p>a765=125.20491077</p> <p>a812=111.15034943</p> <p>a912=111.5212865</p> <p>a1012=111.04745539</p> <p>a1121=116.02463418</p> <p>a1253=111.31039603</p> <p>a1353=111.80619472</p> <p>a1465=114.13562036</p> <p>d4321=-0.99263492</p> <p>d5321=179.70831705</p> <p>d6534=-48.35539388</p> <p>d7653=4.79650757</p> <p>d8123=-120.42872281</p> <p>d9128=120.79330392</p> <p>d10128=-118.56811663</p> <p>d11218=59.68533992</p> <p>d12532=-109.46552183</p> <p>d135312=116.99431106</p> <p>d14657=178.90224802</p>	<p>C</p> <p>C,1,r21</p> <p>C,2,r32,1,a321</p> <p>C,3,r43,2,a432,1,d4321,0</p> <p>C,4,r54,3,a543,2,d5432,0</p> <p>H,1,r61,2,a612,3,d6123,0</p> <p>H,1,r71,2,a712,3,d7123,0</p> <p>H,2,r82,1,a821,6,d8216,0</p> <p>H,3,r93,4,a934,5,d9345,0</p> <p>H,4,r104,3,a1043,2,d10432,0</p> <p>H,4,r114,3,a1143,2,d11432,0</p> <p>O,5,r125,4,a1254,3,d12543,0</p> <p>H,5,r135,4,a1354,3,d13543,0</p> <p>Variables:</p> <p>r21=1.38059238</p> <p>r32=1.38774195</p> <p>r43=1.49799807</p> <p>r54=1.52783081</p> <p>r61=1.08218608</p> <p>r71=1.08433621</p> <p>r82=1.08930577</p> <p>r93=1.08701224</p> <p>r104=1.09637551</p> <p>r114=1.0936891</p> <p>r125=1.20245845</p> <p>r135=1.11210445</p> <p>a321=125.12553124</p> <p>a432=124.42140752</p> <p>a543=110.04169915</p> <p>a612=121.37896143</p> <p>a712=121.17414022</p> <p>a821=117.61790847</p> <p>a934=116.69137776</p> <p>a1043=110.22248183</p> <p>a1143=111.88768632</p> <p>a1254=124.49033437</p> <p>a1354=114.22309892</p> <p>d4321=-177.77607033</p> <p>d5432=104.96227666</p> <p>d6123=-179.12660905</p> <p>d7123=0.68476792</p> <p>d8216=0.14655062</p> <p>d9345=-72.25566787</p> <p>d10432=-14.1149147</p> <p>d11432=-135.74421587</p> <p>d12543=113.28229026</p> <p>d13543=-64.9051291</p>	<p>C</p> <p>C,1,r21</p> <p>C,2,r32,1,a321</p> <p>C,3,r43,2,a432,1,d4321,0</p> <p>C,4,r54,3,a543,2,d5432,0</p> <p>H,1,r61,2,a612,3,d6123,0</p> <p>H,1,r71,2,a712,3,d7123,0</p> <p>H,1,r81,2,a812,3,d8123,0</p> <p>H,3,r93,4,a934,5,d9345,0</p> <p>H,4,r104,3,a1043,2,d10432,0</p> <p>H,4,r114,3,a1143,2,d11432,0</p> <p>O,5,r125,4,a1254,3,d12543,0</p> <p>H,5,r135,4,a1354,3,d13543,0</p> <p>Variables:</p> <p>r21=1.4688656</p> <p>r32=1.30939059</p> <p>r43=1.50593641</p> <p>r54=1.51444414</p> <p>r61=1.09451693</p> <p>r71=1.09460715</p> <p>r81=1.10100216</p> <p>r93=1.09538662</p> <p>r104=1.10226466</p> <p>r114=1.09565066</p> <p>r125=1.20342784</p> <p>r135=1.11355204</p> <p>a321=140.19116329</p> <p>a432=125.13683483</p> <p>a543=114.33978469</p> <p>a612=111.39095244</p> <p>a712=111.46744441</p> <p>a812=110.79534449</p> <p>a934=115.42050083</p> <p>a1043=111.09942543</p> <p>a1143=111.45064399</p> <p>a1254=125.21764055</p> <p>a1354=114.12312902</p> <p>d4321=-179.87915912</p> <p>d5432=-135.7102038</p> <p>d6123=-120.41064437</p> <p>d7123=119.56737975</p> <p>d8123=-0.49165737</p> <p>d9345=43.31586113</p> <p>d10432=104.78960933</p> <p>d11432=-12.13345258</p> <p>d12543=-5.96117338</p> <p>d13543=175.29941511</p>

Table B.1 Optimized Structure Coordinates for Parent Molecules and Radicals from CBS-QB3 Level (Continued)

ccdcjccdo	ccdcjccdo	ccdcjccdo
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
C,4,r54,3,a543,2,d5432,0	C,4,r54,3,a543,2,d5432,0	C,4,r54,3,a543,2,d5432,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0	H,1,r71,2,a712,3,d7123,0
H,1,r81,2,a812,3,d8123,0	H,1,r81,2,a812,3,d8123,0	H,1,r81,2,a812,3,d8123,0
H,2,r92,1,a921,6,d9216,0	H,2,r92,1,a921,6,d9216,0	H,2,r92,1,a921,6,d9216,0
H,4,r104,5,a1045,3,d10453,0	H,3,r103,2,a1032,1,d10321,0	H,3,r103,4,a1034,5,d10345,0
H,4,r114,5,a1145,3,d11453,0	H,4,r114,3,a1143,2,d11432,0	H,4,r114,3,a1143,2,d11432,0
O,5,r125,4,a1254,3,d12543,0	O,5,r125,4,a1254,3,d12543,0	H,4,r124,3,a1243,2,d12432,0
H,5,r135,4,a1354,3,d13543,0	H,5,r135,4,a1354,3,d13543,0	O,5,r135,4,a1354,3,d13543,0
Variables:	Variables:	Variables:
r21=1.50754682	r21=1.49114129	r21=1.49960373
r32=1.31125525	r32=1.37387156	r32=1.3316757
r43=1.47644047	r43=1.39720895	r43=1.50094933
r54=1.52924086	r54=1.44312448	r54=1.53600875
r61=1.09495645	r61=1.09682019	r61=1.09222697
r71=1.09071823	r71=1.09681442	r71=1.09559964
r81=1.09493267	r81=1.09190412	r81=1.09562484
r92=1.0975769	r92=1.08783564	r92=1.0898138
r104=1.09373313	r103=1.08979926	r103=1.08744857
r114=1.09854782	r114=1.08610851	r114=1.09240157
r125=1.20134021	r125=1.22249339	r124=1.09896014
r135=1.11082499	r135=1.11170237	r135=1.17976646
a321=125.64374498	a321=124.86541328	a321=125.16365184
a432=140.12917689	a432=124.81421508	a432=124.19681799
a543=110.2624213	a543=122.46181878	a543=114.05642381
a612=110.75730066	a612=111.00714659	a612=111.60642882
a712=111.21003947	a712=111.00790051	a712=111.08807108
a812=110.6464523	a812=111.95258015	a812=110.95571103
a921=115.50847958	a921=117.00627019	a921=116.11779764
a1045=108.79007381	a1032=117.94770233	a1034=115.9499208
a1145=107.9022073	a1143=120.74044828	a1143=112.29924452
a1254=124.14506211	a1254=124.29537722	a1243=112.00741632
a1354=114.23841703	a1354=115.1840306	a1354=128.0721871
d4321=-179.98326553	d4321=179.99795554	d4321=-179.38721489
d5432=22.39043849	d5432=179.99979244	d5432=121.93967721
d6123=121.25671541	d6123=-121.09353249	d6123=0.32532565
d7123=0.49483111	d7123=121.12980921	d7123=-120.52619799
d8123=-120.17814676	d8123=0.01702366	d8123=121.0099492
d9216=-59.65283569	d9216=58.90466792	d9216=-179.83283933
d10453=122.74532347	d10321=-0.00204678	d10345=-56.30235034
d11453=-120.0635306	d11432=-0.00015895	d11432=-1.38251884
d12543=-112.90323748	d12543=179.99821934	d12432=-120.77249805
d13543=64.9544628	d13543=0.0019525	d13543=18.81854553

Table B.1 Optimized Structure Coordinates for Parent Molecules and Radicals from CBS-QB3 Level (Continued)

cdcccd	cjdcccd	cdcjccdo
C	C	C
C,1,r21	C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
H,1,r51,2,a512,3,d5123,0	H,1,r51,2,a512,3,d5123,0	H,1,r51,2,a512,3,d5123,0
H,1,r61,2,a612,3,d6123,0	H,2,r62,3,a623,4,d6234,0	H,1,r61,2,a612,3,d6123,0
H,2,r72,3,a723,4,d7234,0	H,3,r73,2,a732,1,d7321,0	H,3,r73,4,a734,2,d7342,0
H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0	H,3,r83,4,a834,2,d8342,0
H,3,r93,2,a932,1,d9321,0	O,4,r94,3,a943,2,d9432,0	O,4,r94,3,a943,2,d9432,0
H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0	H,4,r104,3,a1043,2,d10432,0
O,4,r114,3,a1143,2,d11432,0	Variables:	0
Variables:	r21=1.30638592	Variables:
r21=1.32840553	r32=1.5074575	r21=1.30672766
r32=1.49993447	r43=1.51485536	r32=1.46754808
r43=1.51664435	r51=1.07958556	r43=1.53049191
r51=1.08392137	r62=1.09441828	r51=1.08738601
r61=1.08617388	r73=1.09512807	r61=1.09217212
r72=1.08597448	r83=1.10168936	r73=1.1003036
r83=1.10231096	r94=1.2031103	r83=1.10030361
r93=1.09689883	r104=1.11280814	r94=1.19986782
r104=1.11343667	a321=125.02461501	r104=1.11422333
r114=1.2030707	a432=114.02883006	a321=140.7893974
a321=124.49802276	a512=137.97278105	a432=117.08413482
a432=114.65187162	a623=115.18907415	a512=122.12802618
a512=121.45949922	a732=111.57831122	a612=120.68549927
a612=121.86561586	a832=110.66361462	a734=106.20698429
a723=115.67270621	a943=125.04399913	a834=106.20723004
a832=110.93053435	a1043=114.18525658	a943=126.27385316
a932=111.79603027	d4321=139.15785182	a1043=112.78049613
a1043=114.14351677	d5123=179.61319654	d4321=-0.00199019
a1143=125.12009479	d6234=-39.94947675	d5123=-179.98929357
d4321=-132.45180585	d7321=15.28233346	d6123=-0.0073028
d5123=-179.48953002	d8321=-101.6210999	d7342=124.6597616
d6123=0.58774147	d9432=6.78465988	d8342=-124.66000803
d7234=47.11902454	d10432=-174.4995831	d9432=-0.00304072
d8321=108.16042894		d10432=179.99785984
d9321=-8.78217166		
d10432=175.85186039		
d11432=-5.21227409		

Table B.1 Optimized Structure Coordinates for Parent Molecules and Radicals from CBS-QB3 Level (Continued)

cdccjdo	cdcccjdo
C	C
C,1,r21	C,1,r21
C,2,r32,1,a321	C,2,r32,1,a321
C,3,r43,2,a432,1,d4321,0	C,3,r43,2,a432,1,d4321,0
H,1,r51,2,a512,3,d5123,0	H,1,r51,2,a512,3,d5123,0
H,1,r61,2,a612,3,d6123,0	H,1,r61,2,a612,3,d6123,0
H,2,r72,1,a721,5,d7215,0	H,2,r72,3,a723,4,d7234,0
H,3,r83,2,a832,1,d8321,0	H,3,r83,2,a832,1,d8321,0
O,4,r94,3,a943,2,d9432,0	H,3,r93,2,a932,1,d9321,0
H,4,r104,3,a1043,2,d10432,0	O,4,r104,3,a1043,2,d10432,0
Variables:	Variables:
r21=1.37078899	r21=1.32906341
r32=1.39811924	r32=1.50166997
r43=1.44603707	r43=1.53511538
r51=1.08262732	r51=1.08392001
r61=1.08435908	r61=1.08591268
r72=1.08870426	r72=1.08643262
r83=1.08619398	r83=1.09217838
r94=1.22102687	r93=1.09871602
r104=1.11148477	r104=1.17938476
a321=124.60449549	a321=124.15091368
a432=122.4137579	a432=113.92910703
a512=121.51068463	a512=121.43678998
a612=121.11912354	a612=121.78212034
a721=118.25579135	a723=115.76985823
a832=120.74458964	a832=112.28453939
a943=124.07558714	a932=111.71768981
a1043=115.23616028	a1043=128.1303116
d4321=180.	d4321=122.96941499
d5123=180.	d5123=-179.4966453
d6123=0.00007141	d6123=0.72812641
d7215=0.	d7234=-55.43148928
d8321=-0.00009605	d8321=-0.48715138
d9432=-179.99892586	d9321=-119.88805661
d10432=-0.00137625	d10432=18.81680143

Table B.1 Optimized Structure Coordinates for Parent Molecules and Radicals from CBS-QB3 Level (Continued)

internal coordinate	
cdccdo	cjdccdo
Charge = 0 Multiplicity = 1 Redundant internal coordinates found in file. C,0,0.0007610962,0.0000371611,0.0020087845 C,0,0.00018897,-0.0000051958,1.3359333813 H,0,0.931634168,0.0000455875,1.8952571333 H,0,-0.9159463253,-0.0000844242,1.9144369454 H,0,-0.9153123863,-0.0000101836,-0.5805539126 C,0,1.2624739274,0.0001629705,-0.762583502 O,0,1.3275857842,0.0000413898,-1.969372061 H,0,2.1818832011,0.0000365129,-0.1352354251	Charge = 0 Multiplicity = 2 Redundant internal coordinates found in file. C,0,-0.0058830015,-0.0000551258,0.0044300769 C,0,-0.0001691656,-0.0001271574,1.3159217566 C,0,1.2524640229,0.0000561963,2.1172336144 H,0,-0.7060241749,-0.0001201051,-0.8169940236 H,0,-0.9254884754,-0.0002719369,1.899578426 O,0,1.266395128,-0.0000119047,3.3241378757 H,0,2.1861361812,0.0002309324,1.5207165767
cdcjdo	cdcejdo
Charge = 0 Multiplicity = 2 Redundant internal coordinates found in file. C,0,0.0000815816,0.0000646284,0.0004819129 C,0,0.0042286951,0.0003973376,1.3153483307 C,0,1.0672567441,-0.0000844867,2.3334801036 H,0,0.7409057268,-0.0010780131,3.3886006372 O,0,2.2405214982,0.0006401103,2.0340596097 H,0,-0.9197267523,0.0008165582,-0.5774363945 H,0,0.9368925707,-0.0010932863,-0.5610452557	Charge = 0 Multiplicity = 2 Redundant internal coordinates found in file. C,0,0.0004773638,0.0000261755,0.0008559713 C,0,0.0011007672,0.0000269079,1.334318518 C,0,1.2737343688,0.0000140575,2.0818204212 H,0,-0.9211562647,0.0001400894,-0.5691612969 H,0,0.9340173624,0.0000562428,-0.550935901 H,0,-0.9190605424,0.0000948218,1.9177390285 O,0,1.4366336198,0.0000197603,3.2556734601
cdccdo	cjdccdo
Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 1 C,0,0.0026929357,0.0006270978,0.0013355895 C,0,0.003576157,-0.0019632204,1.501358724 C,0,1.0920096839,0.0080458085,2.2668526745 H,0,2.0749907888,0.0027127158,1.8027313681 C,0,1.0772211892,0.0115803862,3.7661382634 C,0,1.9814747084,-1.0198587685,4.4124440685 O,0,2.736879153,-1.7472084595,3.8223085265 H,0,-0.5242926835,0.8770919275,-0.3922270035 H,0,1.018615188,0.0054366659,-0.3999698327 H,0,-0.5150625934,-0.8805626822,-0.3933585355 H,0,-0.9755974433,-0.0149408628,1.9801841571 H,0,1.4083428998,0.9836886123,4.1678924098 H,0,0.0643107305,-0.1285196301,4.1640969066 H,0,1.9139586243,-1.052246862,5.5237557454	Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 2 C,0,0.0017679714,0.0013519295,0.0022019466 C,0,0.0020595768,-0.0026048757,1.3827886295 C,0,1.1372509987,-0.0026581588,2.181016761 C,0,1.1197883184,-0.0549354577,3.6780005133 C,0,1.5178014659,-1.4497711121,4.1578817497 H,0,-0.9221773832,0.0152307233,-0.5610556057 H,0,0.929359036,-0.0063002439,-0.5593149962 H,0,-0.9629671962,0.0062910791,1.8879927913 H,0,2.1137701885,-0.0095617809,1.7035670649 H,0,0.1119076014,0.1586897502,4.0529404904 H,0,1.8244393948,0.6557790496,4.1190306699 O,0,2.5265887941,-1.6996701185,4.7626998503 H,0,0.8016465213,-2.2517084086,3.8736371887

Table B.1 Optimized Structure Coordinates for Parent Molecules and Radicals from CBS-QB3 Level (Continued)

ccjdccdo	ccdcjccdo
Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 2 C,0,0.00022454,-0.000559896,0.0022281912 C,0,0.0025669457,-0.0021408619,1.4710910749 C,0,0.842477165,-0.0016300155,2.4756080096 C,0,0.4536603678,-0.0065361024,3.9304763514 C,0,1.243331623,0.9576803006,4.7908524861 H,0,-0.5179517316,0.8777956949,-0.3952037108 H,0,-0.501389288,-0.8870963654,-0.3985229371 H,0,1.0288202055,0.0106493485,-0.3902906848 H,0,1.9194644471,0.0194578255,2.2767976778 H,0,0.6083165012,-1.0013882281,4.3791834923 H,0,-0.6137124362,0.2037374881,4.0606711292 O,0,2.1820803774,1.6117638723,4.4178055555 H,0,0.8983054957,1.011555725,5.8482325293	Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 2 C,0,0.0017744443,0.0023523301,0.0004670497 C,0,0.0008552099,-0.001778428,1.5080079304 C,0,1.0659881713,-0.0048642657,2.2727775622 C,0,1.4344237752,-0.0094014613,3.7025016874 C,0,0.2816830335,-0.5575015684,4.5447324553 H,0,-0.5300676878,-0.8713534473,-0.3903165078 H,0,1.0188017875,-0.0062947438,-0.3935467476 H,0,-0.5122278832,0.8896266989,-0.3834904397 H,0,-0.9898797807,0.0135730857,1.980113394 H,0,1.6841906344,0.9943663201,4.0579154102 H,0,2.3070898144,-0.6573080068,3.8621212342 O,0,-0.3531897031,0.0975643695,5.3264251906 H,0,0.0423871663,-1.6247503442,4.3506971694
ccdccjdo	ccdccejdo
Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 2 C,0,0.0014335507,0.0000039226,0.0020878791 C,0,0.0016933755,0.0000570593,1.4932291452 C,0,1.1290878364,0.0000063712,2.2784073292 C,0,1.1280827832,0.0000971798,3.6756159099 C,0,2.3451605706,0.0000333618,4.4510705701 H,0,-0.527364026,0.8768362121,-0.3910441542 H,0,-0.5280359644,-0.8764385153,-0.3909929611 H,0,1.0140963961,-0.0003822076,-0.4062850171 H,0,-0.9674351281,0.0001727483,1.9873711284 H,0,2.0984003647,-0.0001134202,1.7803153386 H,0,0.1941824984,0.0002199903,4.2301084236 O,0,2.3833967449,0.0001404949,5.6729658529 H,0,3.2847060051,-0.0000590687,3.8568176605	Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 2 C,0,0.0014113811,-0.0008004308,0.0017182488 C,0,0.0026909092,-0.0007622706,1.5013214315 C,0,1.0919927241,0.0041349076,2.2673225677 C,0,1.0680473418,-0.0092172936,3.7680214811 C,0,1.8125876701,-1.1971425539,4.3955692052 H,0,1.016548951,-0.0020267613,-0.4013375358 H,0,-0.5220862017,0.8773964747,-0.3920571262 H,0,-0.5221056034,-0.8800886094,-0.3896588881 H,0,-0.9754318029,-0.0024330889,1.9819119866 H,0,2.077071879,-0.0113725857,1.8069716566 H,0,0.0509491822,0.0008782449,4.1664566745 H,0,1.5733666699,0.8679368931,4.1957670748 O,0,2.6233141613,-1.8935861502,3.8960316402

Table B.1 Optimized Structure Coordinates for Parent Molecules and Radicals from CBS-QB3 Level (Continued)

cdccdo	cjdccdo
Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 1 C,0,0.0050228123,-0.0020030788,0.0001530271 C,0,-0.0002689939,0.0008512218,1.3285449538 C,0,1.2325013097,0.0035674564,2.1829882834 C,0,1.2231452043,-1.0110741581,3.3102082909 H,0,-0.9172803056,0.004352563,-0.5692344609 H,0,0.9297328956,-0.0120329802,-0.5695700313 H,0,-0.9444875664,-0.0059984129,1.8649635701 H,0,1.3726491092,0.9830038117,2.6689434976 H,0,2.140733586,-0.1525664666,1.5880736919 H,0,2.1705291856,-1.0522815305,3.8937378626 O,0,0.2922851009,-1.7165066105,3.5987280112	Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 2 C,0,-0.0033478062,-0.0006002052,0.0046086875 C,0,-0.0003344435,-0.0023810019,1.3109899227 C,0,1.2361134811,0.0013497062,2.1733185845 C,0,1.1397195406,0.9041397514,3.3859459435 H,0,-0.7279189075,-0.007261056,-0.7956770969 H,0,-0.9488912244,0.0085292947,1.8567667748 H,0,2.127343169,0.2741025525,1.5983220445 H,0,1.440218862,-1.0080703164,2.5646389868 O,0,0.1464502232,1.4847847678,3.737715491 H,0,2.0829199422,0.983929133,3.9710515787
cdcjccdo	cdccjdo
Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 2 C,0,-0.0010579075,-0.0000809481,0.0029430939 C,0,0.0030260249,-0.0000725253,1.3096643713 C,0,0.9343191035,-0.0000955702,2.4438559677 C,0,2.4296479387,-0.0001939652,2.117670223 H,0,-0.9237264825,0.0001175488,-0.5724619821 H,0,0.9364433402,0.0000044227,-0.5573526786 H,0,0.7622812254,-0.8691475029,3.0964046084 H,0,0.762380967,0.8690105004,3.0963588022 O,0,2.9170719531,-0.0003056825,1.0212667373 H,0,3.0701099408,-0.0001676736,3.0294278925	Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 2 C,0,0.0009231799,0.0000325324,0.0019381732 C,0,0.0006523242,-0.00006663475,1.3727271328 C,0,1.1512759074,-0.0000358259,2.1669580634 C,0,1.0957137924,-0.0001432413,3.6119272845 H,0,-0.9219510223,0.0000033559,-0.5640875416 H,0,0.9293478805,0.0001426236,-0.5582958602 H,0,-0.9584269017,-0.0001769782,1.8879397031 H,0,2.138569997,0.0000706048,1.7141140095 O,0,2.0800558264,-0.0001012431,4.3344072972 H,0,0.072845333,-0.0002277127,4.0468278503
cdcccjdo	
Redundant internal coordinates taken from checkpoint file: Charge = 0 Multiplicity = 2 C,0,0.0004006803,0.001935368,0.0027538844 C,0,0.0000702242,-0.0040429229,1.3318038057 C,0,1.2425713106,-0.001937321,2.1751301407 C,0,1.3233599791,1.171238323,3.1618982626 H,0,-0.9242691652,0.0082140285,-0.5627802323 H,0,0.9236013798,-0.002841913,-0.5689838132 H,0,-0.9400963658,0.0163507856,1.8758688055 H,0,2.152803825,-0.0034948238,1.5715342851 H,0,1.2975300613,-0.8895680418,2.8203185896 O,0,0.447084781,1.8597691239,3.5479235433	

Table B.2 Ideal Gas-phase Entropy S° vs. Temperature

T(K)	cdccdo		cjdccdo		cdcjdo	cdccjdo
	SMCPS	SMCPS+VIBIR	SMCPS	SMCPS+VIBIR	SMCPS	SMCPS
50.00	47.23	54.44	48.30	55.51	48.99	48.40
100.00	53.39	60.07	54.50	61.13	55.93	54.39
150.00	57.56	63.66	58.68	64.72	60.52	58.61
200.00	60.91	66.54	62.06	64.72	64.16	62.17
250.00	63.86	66.24	65.03	67.52	67.29	65.36
298.00	66.47	68.70	67.66	70.01	70.00	68.17
400.00	71.60	73.59	72.75	74.87	75.15	73.57
500.00	76.26	78.07	77.26	79.21	79.66	78.26
600.00	80.61	82.29	81.38	83.21	83.76	82.48
700.00	84.68	86.25	85.17	86.90	87.54	86.33
800.00	88.48	89.97	88.67	90.32	91.02	89.85
1000.00	95.41	96.75	94.95	96.45	97.29	96.15
1500.00	109.60	110.63	107.61	108.72	109.94	108.76
2000.00	120.69	121.40	117.35	118.10	119.69	118.46
2500.00	129.68	130.10	125.21	125.62	127.55	126.29
3000.00	137.23	137.36	131.77	131.89	134.12	132.84
3500.00	143.70	143.58	137.39	137.25	139.74	138.45
4000.00	149.36	149.02	142.30	141.92	144.66	143.35
4500.00	154.39	153.84	146.65	146.06	149.01	147.70

Units in cal/mol/K

Table B.2 Ideal Gas-phase Entropy S° vs. Temperature (Continued)

T(K)	cdcccd (trans)		cdcccd (cis)		cjdcccd		ccjdcccd	
	SMCPS	SMCPS +VIBIR	SMCPS	SMCPS +VIBIR	SMCPS	SMCPS +VIBIR	SMCPS	SMCPS+ VIBIR
50.00	50.03	66.14	54.74	53.09	55.27	66.94	51.20	66.12
100.00	56.55	73.32	63.87	64.12	63.94	71.50	57.63	74.69
150.00	61.23	79.28	70.44	66.871	70.10	77.11	62.37	80.84
200.00	65.16	84.19	75.82	70.35	75.28	81.90	66.37	85.83
250.00	68.76	88.49	80.61	73.55	79.95	86.24	70.01	90.14
298.00	72.09	92.29	84.91	76.58	84.18	90.17	73.34	93.90
400.00	79.02	99.86	93.52	83.18	92.66	98.05	80.16	101.26
500.00	85.70	106.88	101.50	89.67	100.47	105.28	86.61	107.98
600.00	92.17	113.56	109.04	95.99	107.78	112.07	92.78	114.32
700.00	98.38	119.90	116.16	102.05	114.63	118.44	98.66	120.31
800.00	104.29	125.91	122.86	107.82	121.04	124.41	104.24	125.95
1000.00	115.26	137.00	135.15	118.50	132.69	133.10	114.53	136.32
1500.00	138.32	160.17	160.61	141.09	156.58	155.50	136.00	157.87
2000.00	156.62	178.50	180.62	159.13	175.22	173.03	152.94	174.84
2500.00	171.59	193.49	196.91	173.96	190.36	187.30	166.76	188.68
3000.00	184.17	206.09	210.58	186.46	203.04	199.27	178.37	200.29
3500.00	195.00	216.92	222.33	197.24	213.92	209.55	188.34	210.27
4000.00	204.49	226.41	232.61	206.69	223.45	218.55	197.08	219.01
4500.00	212.92	234.85	241.74	215.09	231.90	226.54	204.83	226.76
T(K)	cdccjcd		cdccjcd		cdccjcd			
	SMCPS	SMCPS +VIBIR	SMCPS	SMCPS +VIBIR	SMCPS	SMCPS +VIBIR		
50.00	51.28	66.38	51.22	63.18	51.35	68.28		
100.00	57.84	74.99	58.61	71.22	57.95	74.55		
150.00	62.58	81.03	63.91	76.87	62.67	80.56		
200.00	66.57	85.95	68.32	81.58	66.63	85.50		
250.00	70.20	90.23	72.28	85.76	70.24	89.83		
298.00	73.53	93.99	75.87	89.49	73.54	93.63		
400.00	80.34	101.35	83.16	94.00	80.33	101.08		
500.00	86.78	108.09	90.00	101.17	86.75	107.88		
600.00	92.94	114.43	96.51	107.94	92.91	114.25		
700.00	98.81	120.41	102.69	114.33	98.76	120.26		
800.00	104.38	126.06	108.53	120.34	104.31	125.91		
1000.00	114.65	136.42	119.24	131.36	114.55	136.27		
1500.00	136.09	157.95	141.48	154.16	135.91	157.75		
2000.00	153.01	174.91	158.96	172.03	152.79	174.68		
2500.00	166.82	188.74	173.21	186.55	166.58	188.48		
3000.00	178.42	200.34	185.17	198.69	178.17	200.08		
3500.00	188.39	210.32	195.44	209.09	188.13	210.05		
4000.00	197.12	219.05	204.44	218.18	196.85	218.77		
4500.00	204.88	226.81	212.42	226.23	204.60	226.53		

Table B.2 Ideal Gas-phase Entropy S° vs. Temperature (Continued)

T(K)	cdcccd		cjdcdd		cdccjcd		cdccjcd		cdccjcd	
	SMCPS	SMCPS +VIBIR	SMCPS	SMCPS +VIBIR	SMCPS	SMCPS +VIBIR	SMCPS	SMCPS +VIBIR	SMCPS	SMCPS +VIBIR
50.00	50.01	62.95	51.20	61.76	51.24	62.42	50.96	58.79	51.26	61.63
100.00	55.90	69.52	57.09	68.98	57.30	70.01	57.54	65.37	57.18	68.94
150.00	59.85	73.99	61.05	73.96	61.46	75.14	62.11	69.94	61.16	73.94
200.00	63.12	77.61	64.35	77.96	64.90	79.14	65.88	73.70	64.45	77.95
250.00	66.11	80.84	67.38	81.47	68.01	82.60	69.25	77.08	67.43	81.43
298.00	68.87	83.76	70.16	84.56	70.84	85.63	72.30	80.13	70.16	84.48
400.00	74.60	89.69	75.86	90.64	76.56	91.60	78.43	83.36	75.73	90.46
500.00	80.07	95.25	81.17	96.15	81.85	97.01	84.09	89.25	80.94	95.88
600.00	85.32	100.56	86.19	101.29	86.85	102.08	89.41	94.78	85.87	100.94
700.00	90.32	105.60	90.91	106.08	91.55	106.83	94.40	99.93	90.52	105.67
800.00	95.06	110.37	95.34	110.57	95.98	111.27	99.07	104.76	94.89	110.10
1000.00	103.80	119.14	103.45	118.73	104.06	119.40	107.58	113.54	102.90	118.17
1500.00	122.05	137.42	120.14	135.49	120.75	136.12	125.01	131.51	119.45	134.79
2000.00	136.46	151.84	133.21	148.58	133.82	149.20	138.61	145.49	132.45	147.80
2500.00	148.23	163.61	143.84	159.21	144.44	159.83	149.66	156.78	143.03	158.40
3000.00	158.11	173.50	152.74	168.12	153.35	168.74	158.91	166.21	151.91	167.28
3500.00	166.61	182.00	160.39	175.77	161.00	176.39	166.86	174.27	159.54	174.92
4000.00	174.05	189.44	167.08	182.46	167.69	183.08	173.80	181.30	166.22	181.60
4500.00	180.66	196.05	173.02	188.40	173.63	189.02	179.97	187.53	172.15	187.53

Units in cal/mol/K

Table B.3 Summary of Enthalpy of Formation, Entropy and Heat Capacity for Parent Molecules and Corresponding Radicals

SPECIES	$\Delta_f H^\circ$	S°	C_p						
			T(K)	298	300	400	500	600	800
cdcdo	-16.85	68.70	15.90	19.53	22.78	25.55	29.85	32.91	37.33
cjdcdo	42.91	70.01	15.98	19.18	21.85	24.05	27.34	29.60	32.79
cdcjdo	43.87	70.00	16.16	19.00	21.48	23.59	26.90	29.31	32.94
cdccjdo	21.53	68.17	16.87	19.87	22.24	24.16	27.12	29.32	32.78
cdccccdo trans	-27.58	92.29	26.00	31.85	37.31	42.11	49.82	55.55	64.40
cdccccdo cis	-26.28	76.58	25.58	31.96	37.78	42.80	50.60	56.26	64.86
cjdcgccdo	7.49	90.17	25.89	31.91	37.12	41.5	48.29	53.26	60.91
ccjdcgccdo	28.5	93.90	25.58	30.78	35.69	39.99	46.91	52.05	59.92
cdccjccdo	29.9	93.99	25.58	30.83	35.72	40.02	46.90	52.01	59.86
cdcccejdo	-1.83	89.49	23.65	31.55	36.91	41.52	48.74	54.04	62.07
cdcccjdo	9.38	93.63	25.87	31.13	35.95	40.17	46.91	51.94	59.75
cdcccdo	-20.46	83.76	19.81	24.78	29.26	33.10	39.12	43.55	50.33
cjdcgccdo	38.74	84.56	20.66	24.90	28.62	31.79	36.76	40.42	46.01
cdcjccdo	35.83	85.63	20.28	24.47	28.22	31.45	36.53	40.27	45.97
cdccjdo	5.93	80.13	18.57	25.38	29.57	33.06	38.41	42.28	48.10
cdcccjdo	16.78	84.48	20.38	24.51	28.21	31.37	36.35	40.02	45.72

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