ABSTRACT

THERMOCHEMISTRY OF VINYL ALCOHOL AND VINYL ETHER RADICALS AND KINETIC ANALYSIS OF NEOPENTYL RADICAL REACTION WITH MOLECULAR OXYGEN

by
Chol-han Kim

Vinyl alcohols and ethers are important intermediates in low-temperature combustion processes, such as in the initial stages of combustion and in the atmospheric photochemical oxidation of hydrocarbons. Knowledge of the thermodynamic parameters for these species is central to understanding and predicting their reaction pathways, rate constants, and equilibrium constants. The rapid interconversion of conformers and the instability of vinyl alcohols and ethers lead to complexities in studies of these species.

In this work, enthalpy, $\Delta H^\circ_{f\ 298}$, entropy, S°_{298}, and heat capacities, $C_p(T)$, are determined for vinyl alcohol and vinyl methyl ether and the radicals corresponding to loss of a H atom from these two parent molecules by using density functional and *ab initio* calculation methods. The enthalpies of formation are evaluated at four calculation levels using three different working reactions. Entropies (S°_{298}) and heat capacities ($C_p(T)$, $300 \leq T/K \leq 5000$) are calculated using the rigid-rotor-harmonic-oscillator approximation based on frequencies and moments of inertia of the optimized B3LYP/6-31g(d,p) structures. Contributions to entropy and heat capacity from internal rotation are estimated with the B3LYP/6-31g(d,p) level calculations for rotation barrier estimations. Hydrogen Bond Increment groups (HBI) is derived from data obtaining data.

Thermodynamic properties on reactants, intermediates, products and important transition states are calculated and a thermochemical kinetic analysis performed for reaction of neopentyl radical with O_2. The reaction forms a chemically $C_3CC{=}O$ + OH

activated $C_3CCOO\bullet$ adduct, which can be stabilized, dissociate back to reactants to or isomerize to a hydroperoxide alkyl radical. The isomer can dissociate to CH_3 + C=C(C)COOH, to a cyclic ether (C_2CyCCOC) + OH, and to OH + CH_2O + C=C(C_2), isomerize back to the peroxy, or further react with O_2. Kinetics are analyzed with Quantum RRK theory for k(E) coupled with modified strong collision analysis of Gilbert et al for fall-off.

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by
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A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
In Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemical Engineering

Department of Chemical Engineering

January 2002

APPROVAL PAGE

THERMOCHEMISTRY OF VINYL ALCOHOL AND VINYL ETHER RADICALS AND KINETIC ANALYSIS OF NEOPENTYL RADICAL REACTION WITH MOLECULAR OXYGEN

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This thesis is dedicated to my family
For their unending love and encouragement

ACKNOWLEDGMENT

I start by expressing my sincere appreciation to my advisor, Dr. Joseph Bozzelli, for his dedication, patience, and wisdom throughout the length of this study and the preparation of this thesis, and without whose guidance this research would not have been possible. I am grateful to Dr. Dana Knox and Dr. Michael Huang, who served as my committee members, for their inspirational and timely support, technical expertise, and acuity throughout the duration of the project.

Thank you to my family, good friends(Samuel, Shim, Park, Chad, Zhu, Sun, Jin, Lee, Jung,) and my special person (Sun h, Park).

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CHAPTER 1

INTRODUCTION

Vinyl alcohols and methyl vinyl ethers are often intermediates, and products in the oxidation and combustion of hydrocarbons. The thermochemical property data on these vinyl alcohols and methyl vinyl ethers is important for understanding their stability, reaction paths, and kinetics. Enthalpy ($\Delta H^\circ_{f\ (298)}$), Entropy ($S^\circ_{298}$), and Heat capacities ($C_p(T)$, $10 \leq T/K \leq 5000$), are determined for $CH_2{=}CHOH$, $C{\cdot}H{=}CHOH$, $CH_2{=}C{\cdot}OH$, $CH_2{=}CHOCH_3$, $C{\cdot}H{=}CHOCH_3$, $CH_2{=}C{\cdot}OCH_3$, and $CH_2{=}CHOC{\cdot}H_2$. Molecular structures, vibration frequencies, entropy (S°_{298}), and heat capacities ($C_p(T)$, $10 \leq T/K \leq 5000$) are determined at the B3LYP/6-31g(d,p) density functional calculation level. Single point calculation for enthalpies is performed at the B3LYP/6-311+G(3df,2p), B3LYP/6-31G(d'), and the composite CBS-Q//B3LYP/6-31G(d,p) levels. Enthalpies of formation ($\Delta H^\circ_{f\ (298)}$) are determined at each calculation level using three different working reactions. Standard entropy and heat capacity ($C_p(T)$, $10 \leq T/K \leq 5000$) from vibrational, translational, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation. Potential barriers for internal rotation are calculated at the B3LYP/6-31g(d,p) level, and hindered internal rotational contributions to entropy and heat capacity are calculated.

The $\Delta H^\circ_{f\ (298)}$ values show that the syn conformations of vinyl alcohol ($CH_2{=}CHOH$) and methyl vinyl ether ($CH_2{=}CHOCH_3$) are more stable than their anti forms. The recommended ideal gas phase $\Delta H^\circ_{f\ (298)}$ calculated in this study are: –29.71 ± 0.15, -27.96 ± 0.14 (Syn, Anti) of $CH_2{=}CHOH$, 32.34, 37.51 of $C{\cdot}H{=}CHOH$, 26.37

± 0.63, 30.40 ± 0.14 of $CH_2{=}C{\cdot}OH$ -25.02 ± 0.42, -23.48 ± 0.45 for $CH_2{=}CHOCH_3$, 36.94 ± 0.48, 43.54 ± 0.47 for $C{\cdot}H{=}CHOCH_3$, 32.19 ± 0.46 , 36.52 ± 0.46 for $CH_2{=}C{\cdot}OCH_3$, and 21.84, 26.28 for $CH_2{=}CHOC{\cdot}H_2$ (in kcal/mol). The $O/C_D/H$ and $O/C/C_D$ groups (for group additivity) are evaluated from the syn configurations of vinyl alcohol ($CH_2{=}CHOH$) and methyl vinyl ether ($CH_2{=}CHOCH_3$) and compared with literature data.

Neopentyl radical reaction with oxygen, which has a several reaction channel and makes a variety product, is estimated by computational chemistry method. Thermodynamic properties on reactants, intermediates, products and important transition states are calculated and a thermochemical kinetic analysis performed for reaction of neopentyl radical with O_2.

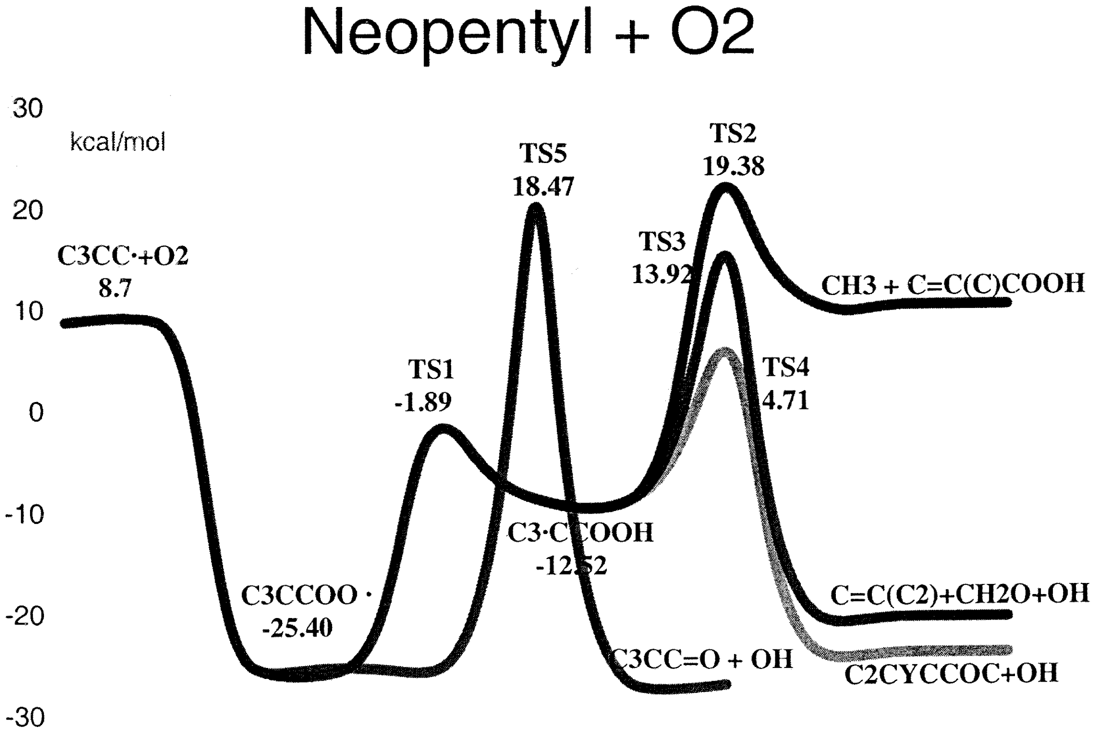


Figure 1. 1 Overview Schematic of Neopentyl + O_2 Paths

The reaction forms a chemically activated $C_3CCOO\bullet$ adduct, which can be stabilized, dissociate back to reactants or isomerize to a hydroperoxide alkyl radical and make $C_3CC{=}O$ + OH product. The isomer can dissociate to CH_3 + $C{=}C(C)COOH$, to a cyclic ether ($C_2CyCCOC$) + OH, and to OH + CH_2O + $C{=}C(C_2)$, isomerize back to the peroxy, or further react with O_2. Kinetics are analyzed with Quantum RRK theory for k(E) coupled with modified strong collision analysis of Gilbert et al for fall-off.

An elementary reaction mechanism with microscopic reversibility of 58 reactions and 39 species is constructed to model experimental data in the literature focusing on this reaction system. The mechanism includes addition of a second O_2 to the hydroperoxy alkyl isomer and subsequent reactions of this adduct. Kinetic parameters for intermediate and product formation channels of neopentyl + O_2 system are presented versus temperature and pressure and are shown to vary from previous analysis. Reaction flux analysis shows that: neopentyl + O_2, the adduct $C_3CCOO\bullet$, and the isomer $C_3\bullet CCOOH$, exist in near equilibrium with slower reactions of the isomer responsible for product formation.

CHAPTER 2

THERMOCHEMISTRY OF VINYL ALCOHOL AND VINYL ETHER RADICALS

2.1 Overview

Vinyl alcohols and ethers are often intermediates, and products in the oxidation and combustion of hydrocarbons. The thermochemical property data on these vinyl alcohols and ethers is important for understanding their stability, reaction paths, and kinetics. Enthalpy ($\Delta H^\circ_{f\,298}$), Entropy (S°_{298}), and Heat capacities ($C_p(T)$, $300 \leq T/K \leq 5000$), are determined for $CH_2{=}CHOH$, $C{\cdot}H{=}CHOH$, $CH_2{=}C{\cdot}OH$, $CH_2{=}CHOCH_3$, $C{\cdot}H{=}CHOCH_3$, $CH_2{=}C{\cdot}OCH_3$, and $CH_2{=}CHOC{\cdot}H_2$. Molecular structures, vibration frequencies, entropy (S°_{298}), and heat capacities ($C_p(T)$, $300 \leq T/K \leq 5000$) are determined at the B3LYP/6-31g(d,p) density functional calculation level. Single point calculation for enthalpies is performed at the B3LYP/6-311+G(3df,2p), B3LYP/6-31G(d'), and the composite CBS-Q//B3LYP/6-31G(d,p) levels. Enthalpies of formation ($\Delta H^\circ_{f\,298}$) are determined at each calculation level using three different working reactions. Standard entropy and heat capacity ($C_p(T)$, $300 \leq T/K \leq 5000$) from vibrational, translational, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation. Potential barriers for internal rotation are calculated at the B3LYP/6-31g(d,p) level, and hindered internal rotational contributions to entropy and heat capacity are calculated.

The $\Delta H^\circ_{f\,(298)}$ values show that the syn conformations of vinyl alcohol ($CH_2{=}CHOH$) and vinyl methyl ether ($CH_2{=}CHOCH_3$) are more stable than their anti forms. The recommended ideal gas phase $\Delta H^\circ_{f\,298}$ calculated in this study are : –29.71

± 0.07, -27.96 ± 0.06 (Syn, Anti) of CH_2=CHOH, 32.34, 37.51 of C·H=CHOH, 26.37 ± 0.26, 30.40 ± 0.06 of CH_2=C·OH -25.02 ± 0.18, -23.48 ± 0.19 for $CH_2=CHOCH_3$, 36.94 ± 0.20 , 43.54 ± 0.19 for C·H=$CHOCH_3$, 32.19 ± 0.19 , 36.52 ± 0.19 for CH_2=C·OCH_3, and 21.84, 26.28 for CH_2=CHOC·H_2 (in kcal/mol). The O/C_D/H and O/C/C_D groups (for group additivity) are evaluated from the anti configurations of vinyl alcohol (CH_2=CHOH) and vinyl ether ($CH_2=CHOCH_3$) and compared with literature data.

2.2 Background

A limited number of experimental and theoretical calculations have been reported on vinyl alcohols and methyl vinyl ether. The rapid interconversion of conformers and the instability of vinyl alcohols and ethers lead to complexities in studies of these species. Experimental and theoretical studies on heats of formation ($\Delta H°_{f\ 298}$) of vinyl alcohols have been reported by several research groups. Turecek et al.[3] reported $\Delta H°_{f\ 298}$ of CH_2=CHOH to be –30.59 kcal/mole (-128 kJ/mol) by experimental study. Holmes and Lossing.[4] reported $\Delta H°_{f\ 298}$of CH_2=CHOH to be –29.87 kcal/mole (-125 ± 8.4 kJ/mol) by experimental study Holmes et al.[5] reported $\Delta H°_{f\ 298}$of CH_2=CHOH to be –26.59 kcal/mole (-111 ± 8.4 kJ/mol) by experimental study. Takahiro Yamada[6] has reported $\Delta H°_{f\ 298}$of CH_2=CHOH to be –29.95 (kcal/mole) by theoretical study. Li zhu[7] has reported $\Delta H°_{f\ 298}$of syn-CH_2=CHOH to be –30.59 (kcal/mole) by theoretical study. Turecek et al.[8] reported the $\Delta H°_{f\ 298}$of syn-vinyl alcohol as –29.6 (kcal/mole) using G2(MP2). Brian et al.[9] reported the $\Delta H°_{f\ 298}$of syn-vinyl alcohol as –29.6 (kcal/mole) using G2(MP2).

In this work, enthalpy, $\Delta H^\circ_{f\ 298}$, entropy, S°_{298}, and heat capacities, $C_p(T)$, are determined for vinyl alcohol and vinyl methyl ether and the radicals corresponding to loss of a H atom from these two parent molecules by using density functional and ab initio calculation methods. The enthalpies of formation are evaluated at four calculation levels using three different working reactions. Entropies (S°_{298}) and heat capacities ($C_p(T)$, $300 \leq T/K \leq 5000$) are calculated using the rigid-rotor-harmonic-oscillator approximation based on frequencies and moments of inertia of the optimized B3LYP/6-31g(d,p) structures. Contributions to entropy and heat capacity from internal rotation are estimated with the B3LYP/6-31g(d,p) level calculations for rotation barrier estimations.

2.3 Computational Methods

2.3.1 Selection of Method

Structural parameters are optimized at the B3LYP/6-31g(d,p) level theory. The harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. These optimized structures are used to obtain total electronic energies at density functional B3LYP/6-31g(d,p), B3LYP/6-311+G(3df,2p), ab initio QCISD(T)/6-31g(d,p), and CBS-Q//B3LYP/6-31G(d,p) calculation levels [11-13].

B3LYP/6-31g(d,p) is chosen because it is reported to yield accurate geometry and reasonable energies [14-18]. Comparison of calculation results from B3LYP/6-31g(d,p) level against data from higher level calculation levels for $\Delta H^\circ_{f\ 298}$ will provide some calibration of the B3LYP/6-31g(d,p) values (with similar working reactions) for larger molecules, where this may be one of the few calculation methods available. B3LYP/ 6-311+G(3df,2p) is chosen to see if this larger basic set results in an improvement to the B3LYP/6-31g(d,p) method [14]. QCISD-(T)/6-31G(d,p) is a configuration interaction method, but with economical basis set.[19,20] The CBS-Q//B3LYP/6-31G(d,p) calculation is a high level composite method with empirical corrections. The CBSQ method has been shown to yield reliable $\Delta H^\circ_{f\ 298}$ values for small molecules.[21-24] B3LYP/6-31g(d,p) harmonic vibrational frequencies. These calculations are referred to as CBS-Q//B3LYP/6-31G(d,p). All calculations are performed using the Gaussian 94 [25] and the Gaussian 98 program [26].

2.3.2 Enthalpies of Formation ($\Delta H^\circ_{f\,298}$)

Standard enthalpies of formation ($\Delta H^\circ_{f\,298}$) are estimated using total energies obtained by the B3LYP/6-31g(d,p), B3LYP/6-311+G(3df,2p), ab initio QCISD(T)/6-31g(d,p), and CBS-Q//B3LYP/6-31G(d,p) calculation methods and three working reactions which are isodesmic. Total energies are corrected by zero-point vibration energies (ZPVE), that are scaled by 0.9806 as recommended by Scott et al [27]. Thermal correction, 0 K to 298.15 K, is calculated to estimate $\Delta H^\circ_{f\,298}$ at 298.15K [28].

The method of isodesmic reactions relies on the similarity of bonding environment in the reactants and products that leads to cancellation of systematic errors in the density functional calculations. The following reactions are selected to determine $\Delta H^\circ_{f\,298}$ of $CH_2{=}CHOH$:

$$CH_2{=}CHOH + CH_3CH_3 \rightarrow CH_3CH_2OH + CH_2{=}CH_2$$

$$CH_2{=}CHOH + CH_4 \rightarrow CH_3OH + CH_2{=}CH_2$$

$$CH_2{=}CHOH + CH_3CH_2CH_3 \rightarrow CH_3CH_2OH + CH_2{=}CHCH_3.$$

Density functional calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and enthalpy of reaction ΔH°_{rxn} is calculated. The known calculated ΔH°_{rxn} and enthalpies of formation of the three standard compounds in the working reaction, allow enthalpy of formation of the target molecule to be obtained.

2.3.3 Entropies (S°_{298}), Heat Capacities ($C_p(T)$), and Hindered Rotation Contribution to Thermodynamic Parameters.

Entropies (S°_{298}) and heat capacities ($C_p(T)$) are calculated using the geometry, symmetry, frequencies and moments of inertia of the B3LYP/6-31g(d,p) optimized structures with values summarized in Table 2.1 and Table 2.2. Contributions to entropy and heat capacity from internal rotations about C-O bonds are determined using rotation potential curves from the B3LYP/6-31g(d,p) calculation level.

A technique for calculation of thermodynamic functions from hindered rotations with arbitrary potentials is used to calculate hindered internal rotor contributions to the vinyl alcohols and ethers.[29, 30] This technique employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix on the basis of wave functions of free internal rotor, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix. In this work, the torsional potential calculated at discrete torsional angles is represented by a truncated Fourier series.

$$V(\emptyset) = a_0 + a_1\cos(\emptyset) + a_2\cos(2\emptyset) + a_3\cos(3\emptyset)\ \ a_4\cos(4\emptyset) + a_5\cos(5\emptyset)$$

$$+ b_1\sin(\emptyset) + b_2\sin(2\emptyset) + b_3\sin(3\emptyset)\ b_4\sin(4\emptyset) + b_5\sin(5\emptyset)\text{kimch}$$

The values of the coefficients a_i and b_i are calculated to provide the minima and maxima of the torsional potentials with allowance of a shift of the theoretical extreme angular positions.

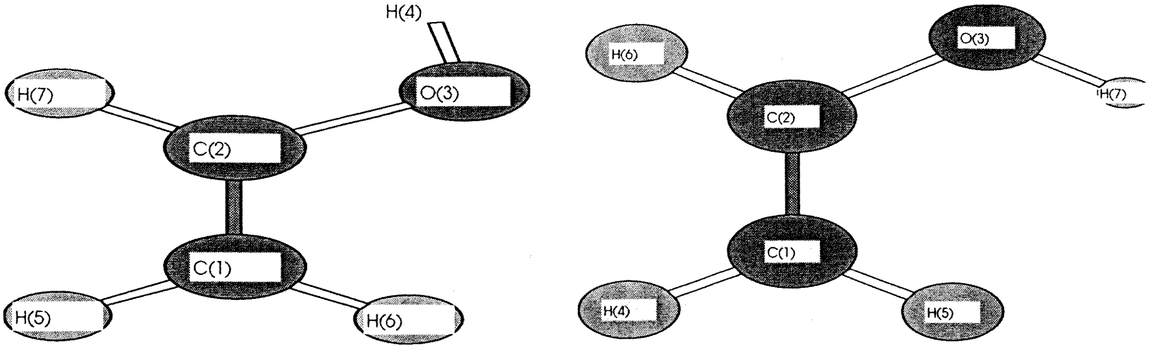
2.4 Results and Discussion

2.4.1 Geometries and Vibrational Frequencies

Illustrations of the optimized geometries at the B3LYP/6-31g(d,p) density functional calculation level for $CH_2=CHOH$, $C\cdot H=CHOH$, $CH_2=C\cdot OH$, $CH_2=CHOCH_3$, $C\cdot H=CHOCH_3$, $CH_2=C\cdot OCH_3$, and $CH_2=CHOC\cdot H_2$ are presented in Figures 2.1 through 2.7 and structure parameters are listed in Appendix A Tables A1 through A7. Trends in bond lengths are illustrated in scheme 1.

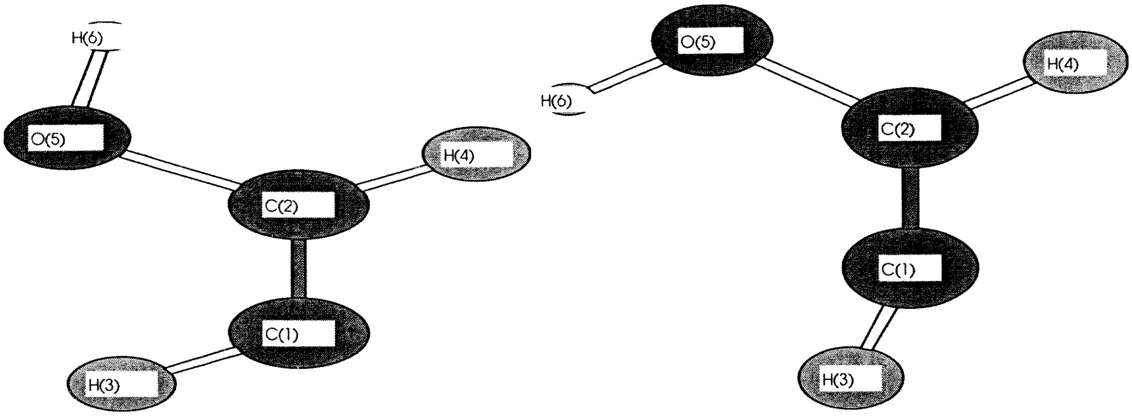
Scheme 1	**Bond Lengths**		
Vinyl alcohol species	**C=C (Å)**	**C=C--O (Å)**	**O--H (Å)**
Syn $CH_2=CHOH$	1.334	1.362	0.968
Syn $C\cdot H=CHOH$	1.315	1.378	0.968
Syn $CH_2=C\cdot OH$	1.322	1.342	0.954
Anti $CH_2=CHOH$	1.331	1.369	0.964
Anti $C\cdot H=CHOH$	1.315	1.380	0.965
Anti $CH_2=C\cdot OH$	1.322	1.340	0.968
Methyl Vinyl ether species	**C=C (Å)**	**C=C--O (Å)**	**O--CH_3 (Å)**
Syn $CH_2=CHOCH_3$	1.336	1.358	1.420
Syn $C\cdot H=CHOCH_3$	1.318	1.371	1.422
Syn $CH_2=C\cdot OCH_3$	1.324	1.316	1.445
Syn $CH_2=CHOC\cdot H_2$	1.334	1.369	1.362
Anti $CH_2=CHOCH_3$	1.332	1.363	1.420
Anti $C\cdot H=CHOCH_3$	1.316	1.374	1.423
Anti $CH_2=C\cdot OCH_3$	1.323	1.331	1.437
Anti $CH_2=CHOC\cdot H_2$	1.332	1.367	1.364

· denotes radical site.



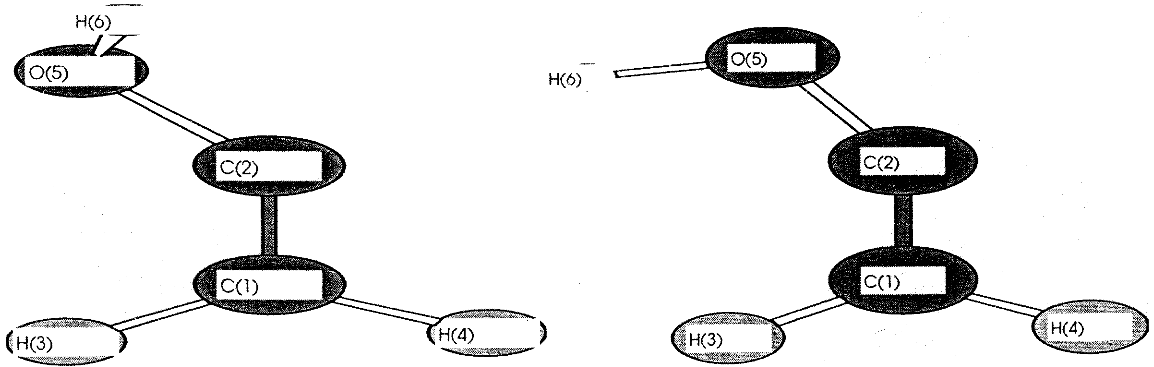
(a) Anti CH_2=CHOH (b) Syn CH_2=CHOH

Figure 2.1 B3lyp/6-31G(d,p) optimized geometries of syn CH_2=CHOH and anti CH_2=CHOH



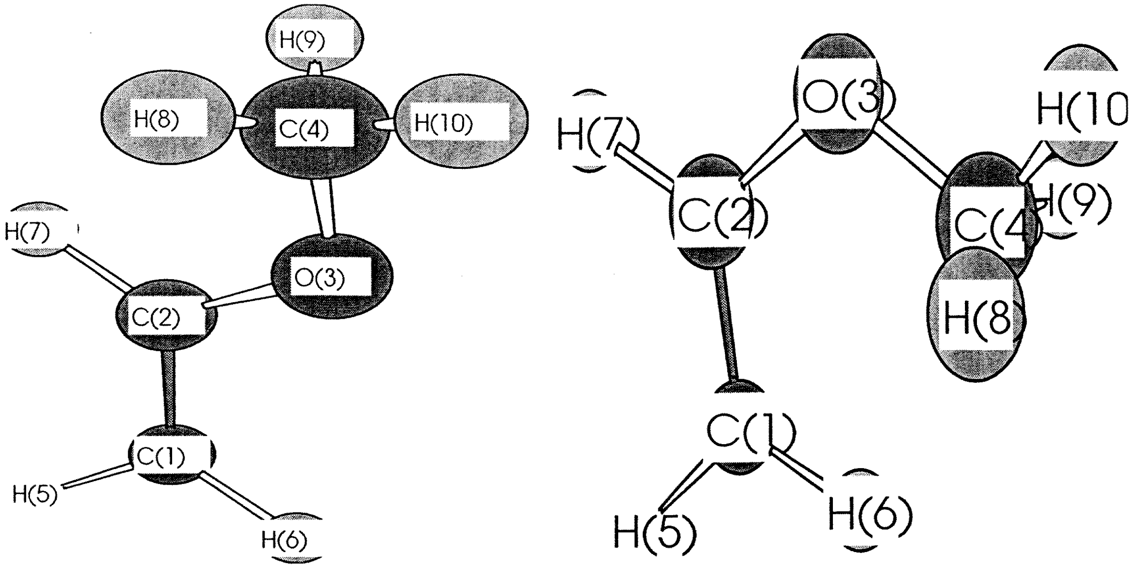
(a)Anti C·H=CHOH (b) Syn C·H=CHOH

Figure 2.2 B3lyp/6-31G(d,p) optimized geometries of syn C·H=CHOH and anti C·H=CHOH



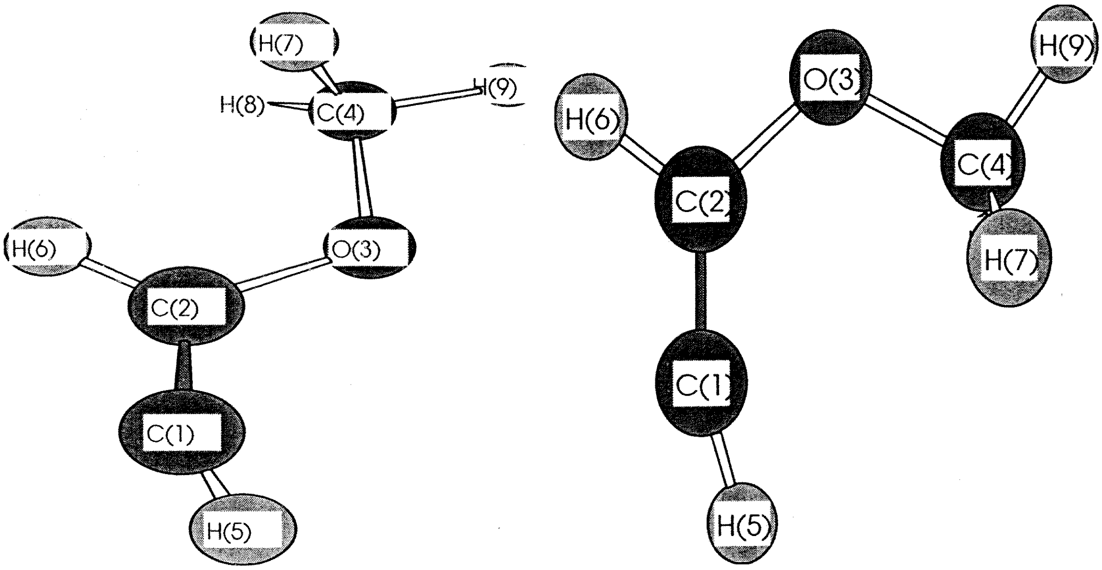
(a) Anti CH_2=C·OH (b) Syn CH_2=C·OH

Figure 2.3 B3lyp/6-31G(d,p) optimized geometries of syn CH_2=C·OH, anti CH_2=C·OH



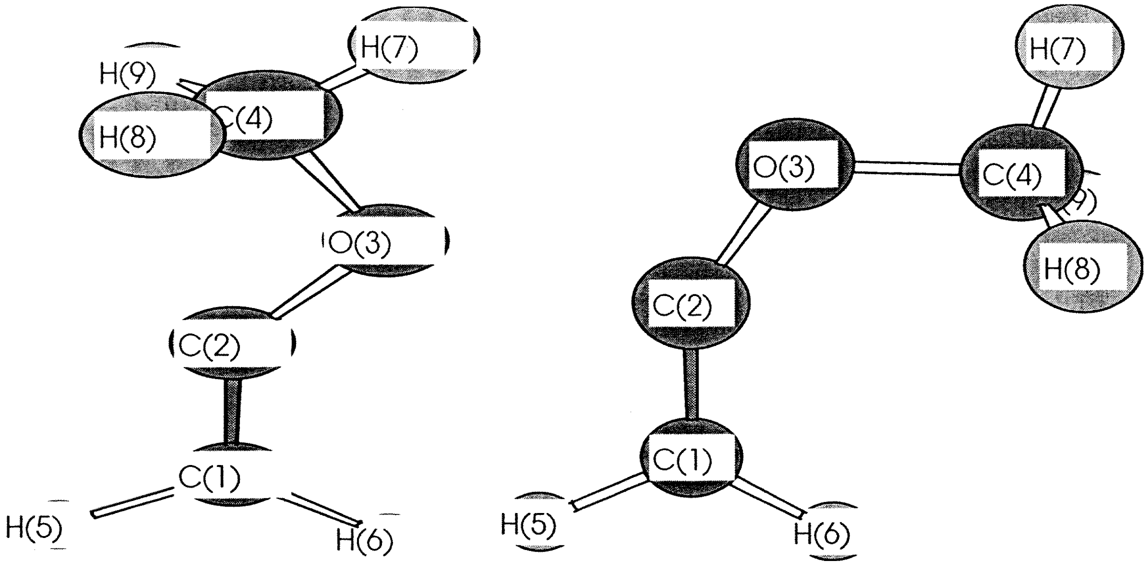
(a) Anti $CH_2=CHOCH_3$ (b) Syn $CH_2=CHOCH_3$

Figure 2.4 B3lyp/6-31G(d,p) optimized geometries of syn $CH_2=CHOCH_3$ and anti $CH_2=CHOCH_3$



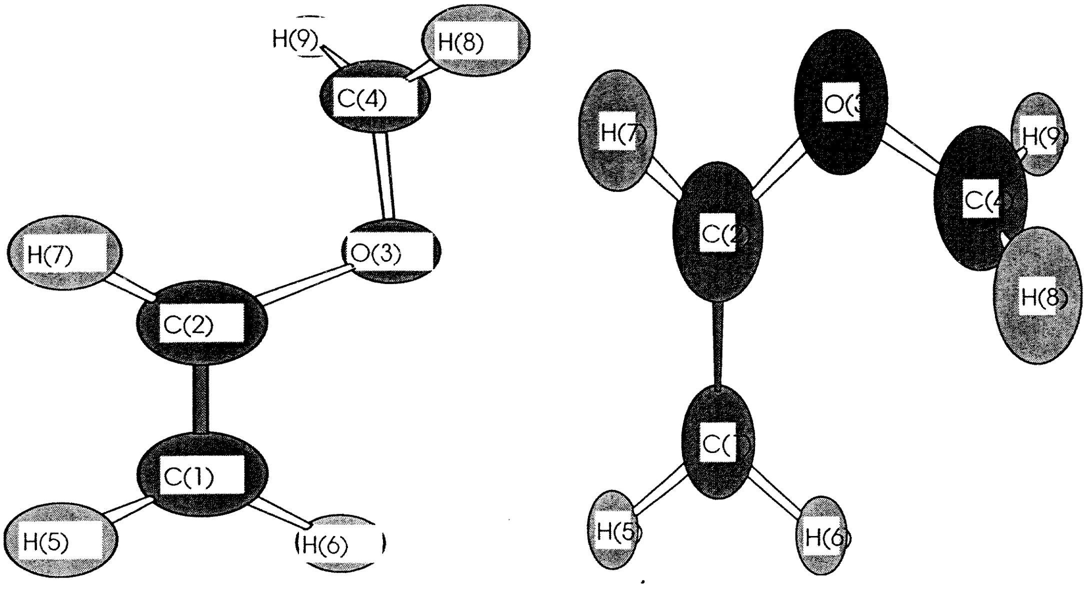
(a) Anti $C{\cdot}H=CHOCH_3$ (b) Syn $C{\cdot}H=CHOCH_3$

Figure 2.5 B3lyp/6-31G(d,p) optimized geometries of syn $CH_2=CHOCH_3$, anti $CH_2=CHOCH_3$ and $C{\cdot}H=CHOCH_3$



(a) Anti $CH_2{=}C{\cdot}OCH_3$ (b) Syn $CH_2{=}C{\cdot}OCH_3$

Figure 2.6 B3lyp/6-31G(d,p) optimized geometries of syn $CH_2{=}C{\cdot}OCH_3$ and anti $CH_2{=}C{\cdot}OCH_3$



(a) Anti $CH_2{=}CHOC{\cdot}H_2$ (b) Syn $CH_2{=}CHOC{\cdot}H_2$

Figure 2.7 B3lyp/6-31G(d,p) optimized geometries of syn $CH_2{=}CHOC{\cdot}H_2$ and anti $CH_2{=}CHOC{\cdot}H_2$

The vibrational frequencies and moments of inertia for vinyl alcohols, methyl vinyl ethers, and radical species are listed in Tables 2.1 and 2.2 respectively.

Table 2.1 Vibration Frequencies [a] (cm^{-1})

Species	V1[b]	v2	v3	v4	v5	v6	v7	v8	v9	v10	v11	v12
	V13	v14	v15	v16	v17	v18	v19	v20	v21	v22	v23	v24
Syn CH_2=CHOH	243.57	481.52	717.39	838.01	960.04	981.89	1155.98	1295.08	1358.71	1450.47	1756.47	3151.52
	3185.4	3277.88	3856.63									
Syn C·H=CHOH	207.6	442.39	593.37	821.55	878.58	1092.72	1253.51	1342.32	1714.41	3127.9	3311.28	3832.25
Syn CH_2=C·OH	340.03	442.29	634.64	815.14	963.17	1139.91	1229.54	1420.83	1733.89	3119.72	3245.01	3790.91
Syn CH_2=CHOCH_3	21.31	177.65	310.03	532.39	700.47	868.93	881.51	978.46	1114.68	1181.76	1185.09	1266.82
	1327.04	1444.04	1494.76	5000.53	1517.29	1720.52	3019.92	3087.09	3096.97	3133.72	3178.03	3247.72
Syn C·H=CHOCH_3	56.7	167.01	312.21	494.17	588.3	808.68	873.27	1005.87	1153.75	1174.65	1226.81	1336.91
	1485.33	1502.91	1515.55	1688.85	3011.81	3072.69	3116.66	3149.19	3306.4			
Syn CH_2=C·OCH_3	114.07	144.73	319.25	484.71	669.97	821.69	894.38	1055.96	1156.47	1172.02	1246.97	1417.52
	1482.75	5000.96	1512.11	1722.86	3043.72	3117.46	3118.75	3164.62	3241.92			
Syn CH_2=CHOC·H_2	92.68	268.1	322.42	538.07	574.45	702.9	852.33	897.11	975.14	1125.65	1213.99	1309.24
	1348.09	1437.2	1489.24	1725.53	3136.19	3163.32	3190.56	3284.12	3290.97			
Anti CH_2=CHOH	481.4	493.36	714.81	818.09	966.55	1001.38	1131.22	1333.94	1366.94	1460.57	1727.07	3162.44
	3204.72	3264.67	3793.42									
Anti C·H=CHOH	445.23	460.62	569.19	801.9	912.93	1072.97	1253.8	1371.12	1678.28	3184.8	3302.7	3796.79
Anti CH_2=C·OH	391.17	442.73	603.66	805.18	993.19	1079.54	1229.61	1441.99	1573.11	3149.29	3243.46	3788.01
Anti CH_2=CHOCH_3	240.45	258.7	322.66	596.68	720.82	826.49	917.37	998.37	1038.19	1182.4	1223.58	1255.51
	1363.51	1439.51	1495.1	5000.81	1521.35	1712.32	3017.84	3078.89	3151.11	3187.57	3201.92	3276.72
Anti C·H=CHOCH_3	225.15	258.86	295.41	551.31	572.34	836.04	906.06	948.62	1158.74	1181.03	1224.38	1340.6
	1477.9	1496.13	1518.1	1661.19	3016.78	3076.28	3153.23	3175.3	3320.65			
Anti CH_2=C·OCH_3	102.21	198.79	252.08	551.73	588.91	762.06	897.37	1003.36	1158.57	1170.4	1199.16	1415.8
	1474.41	1495.75	1510.74	1730.48	3040.92	3114.26	3115.97	3173.81	3240.01			
Anti CH_2=CHOC·H_2	213.6	311.45	357.18	584.37	651.12	715.06	851.65	913.92	983.2	1101.86	1205.14	1282.47
	1382.36	1430.49	1491.15	1701.65	3139.67	3190.12	3218.58	3280.68	3289.43			

[a] Frequencies are calculated at the B3LYP/6-31G(d,p) level of theory. [b] Torsional frequencies. These frequencies are not included in the calculation of entropies S°_{298} and heat capacities $C_p(T)$. 1. Units: 1/cm 2. C· represents radical on preceding carbon atom.

Table 2.2 Momentsof Inertia[a]

Species	Moments of Inertia		
	Ia[b]	Ib	Ic
Syn $CH_2{=}CHOH$	28.2290	173.6190	201.8470
Syn $C{\cdot}H{=}CHOH$	26.0370	161.9890	188.0260
Syn $CH_2{=}C{\cdot}OH$	17.2070	180.2350	194.9000
$CH_2{=}CHO{\cdot}$	26.9670	158.2080	185.1750
Syn $CH_2{=}CHOCH_3$	46.7466	394.0327	429.2498
Syn $C{\cdot}H{=}CHOCH_3$	42.4310	381.6830	412.6040
Syn $CH_2{=}C{\cdot}OCH_3$	46.1670	395.8880	407.4800
Syn $CH_2{=}CHOC{\cdot}H_2$	38.5220	379.6660	417.4810
Anti $CH_2{=}CHOH$	29.7487	171.9546	201.7033
Anti $C{\cdot}H{=}CHOH$	27.9218	159.5073	187.4291
Anti $CH_2{=}C{\cdot}OH$	18.2118	179.2189	193.90168
Anti $CH_2{=}CHOCH_3$	98.0589	285.9532	372.5416
Anti $C{\cdot}H{=}CHOCH_3$	98.0763	263.6003	350.2068
Anti $CH_2{=}C{\cdot}OCH_3$	83.2257	299.2083	370.8866
Anti $CH_2{=}CHOC{\cdot}H_2$	85.64772	281.30477	362.4834

[a]Optimized at the B3lyp/6-31G(d,p) level of theory. [b]Units in amu-Bohr^2.

2.4.2 Enthalpies of Formation ($\Delta H^\circ_{f\,(298)}$)–Vinyl Alcohol and Methyl Vinyl Ether

Enthalpies of formation ($\Delta H^\circ_{f\,(298)}$) and their respective uncertainties for standard species used in the working reactions are adopted from evaluation of literature data or from this work; values for the standard species are listed in Table 2.3. Enthalpies of formation ($\Delta H^\circ_{f\,(298)}$) are estimated using total energies and calculated ΔH°_{rxn} for the listed reactions. The total energies of species are optimized at the B3LYP/6-31G(d,p) level. The ZPVE and the thermal correction to 298.15 K are listed in Table 2.4. The total energies at 298 K from the reaction enthalpies and $\Delta H^\circ_{f\,(298)}$ of the vinyl alcohol and other molecules presented for B3LYP/6-31G(d,p), B3LYP/6-311+G(3df+2p), QCISD(T)/6-31G(d,p), and CBS-Q calculation levels, scaled ZPVE, thermal corrections to 298.15 K are listed in

Table 2.5. ΔH°_{rxn} and $\Delta H^\circ_{f\ (298)}$ for vinyl alcohol, methyl vinyl ether, and the corresponding radicals are presented in Tables 2.6, 2.7.

One reaction used to calculated $\Delta H^\circ_{f\,(298)}$ (CH_2=CHOH) is:

$$CH_2{=}CHOH \quad + \quad CH_3CH_2CH_3 \quad \rightarrow \quad CH_3CH_2OH \quad + \quad CH_2{=}CHCH_3$$

$$\Delta H^\circ_{f\,(298)} \;=\; \Delta H^\circ_{f\,(298)}(CH_3CH_2OH) + \Delta H^\circ_{f\,(298)}(CH_2{=}CHCH_3) \\ -\ (\ \Delta H^\circ_{f\,(298)}(CH_2{=}CHOH) + \Delta H^\circ_{f\,(298)}(CH_3CH_2CH_3)\ )$$

$\Delta H^\circ_{f\ (298)}$ values from the highest level (CBSQ) calculation for vinyl alcohol species are: –29.71 ± 0.15, -27.96 ± 0.14 (Syn, Anti) of CH_2=CHOH, 32.34, 37.51 of C·H=CHOH, 26.37 ± 0.63, 30.40 ± 0.14 of CH_2=C·OH.

Enthalpy values for the methyl vinyl ethers species are: -25.02 ± 0.42, -23.48 ± 0.45 (Syn, Anti) of CH_2=$CHOCH_3$, 36.94 ± 0.48, 43.54 ± 0.47 of C·H=$CHOCH_3$, 32.19 ± 0.46, 36.52 ± 0.46 of CH_2=C·OCH_3, 21.84, 26.28 of CH_2=CHOC·H_2.

The accuracy of the enthalpies of formation obtained theoretically is controlled by several factors: the level of sophistication (method + basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and the choice of the working chemical reaction used for cancellation of calculation errors.

The three reaction of vinyl alcohol and methyl vinyl ether is isodesmic reactions, which conserve bond type on both sides of the reaction and in principle should show more consistent enthalpy values. Also, the rest reaction shows good consistency with a standard deviation of less than ± 0.63. The result shows that the $\Delta H^\circ_{f\,(298)}$ values of syn vinyl alcohol, methyl vinyl ether, and corresponding radicals are lower than that of anti molecules.

Table 2.3 $\Delta H_f^o{}_{298}$ for Standard Species used in Reaction Schemes and Bond Energy Calculations[a]

Species	$\Delta H_f^o{}_{298}$ (kcal/mol)	Species	$\Delta H_f^o{}_{298}$ (kcal/mol)
CH_4	−17.89[b] ± 0.07	$CH_2{=}CH_2$	12.53[h] ± 0.18
CH_3OH	−48.08[c] ± 0.02	$CH_2{=}CHCH_3$	4.87[I] ± 0.08
$CH_3CH_2CH_3$	-25.02[d] ± 0.05	$CH_3C{\cdot}HOH$	−13.34[j] ± 0.84
C_2H_5OH	−56.12[e] ± 0.2	$C{\cdot}H{=}CH_2$	71.46[k] ± 0.05
C_2H_6	−20.24[f] ± 0.29	$CH_3CH_2OCH_3$	-51.71[l] ± 0.05
CH_3OCH_3	-43.99[g] ± 0.05	$CH_2{=}CHO{\cdot}$	-3.93[m] ± 0.13

[a] The uncertainties without superscript are evaluated from reference 37 and 38. [b] Reference 35. [c] Reference 43. [d] Reference 36. [e] Reference 37. [f] Reference 36. [g] Reference 43. [h] Reference 38. [i] Reference 39. [j] Reference 40. [k] Reference 41, [l] Reference 43. [m] Reference 42.

Table 2.4 Total Energy[a], ZPVE, and Thermal Corrections

Species	ZPVE[b]	Sum of elec[c]	Sum of zpe[d]	Thermal. Corr [e]	Total E [f]
Syn CH2=CHOH	0.0560	-153.7517	-153.7565	0.0048	-153.7522
Syn C·H=CHOH	0.0420	-153.0717	-153.0766	0.0049	-153.0721
Syn CH2=C·OH	0.0430	-153.0849	-153.0896	0.0047	-153.0853
Syn CH2=CHOCH3	0.0840	-193.0296	-193.0349	0.0053	-193.0297
Syn C·H=CHOCH3	0.0710	-192.3494	-192.3549	0.0055	-192.3485
Syn CH2=C·OCH3	0.0720	-192.3618	-192.3679	0.0061	-192.3609
Syn CH2=CHOC·H2	0.0700	-192.3785	-192.3846	0.0061	-192.3789
Anti CH2=CHOH	0.0568	-153.7547	-153.7593	0.0046	-153.7547
Anti C·H=CHOH	0.0429	-153.0753	-153.0800	0.0047	-153.0753
Anti CH2=C·OH	0.0430	-153.0849	-153.0896	0.0047	-153.0839
Anti CH2=CHOCH3	0.0855	-193.0317	-193.0374	0.0057	-193.0317
Anti C·H=CHOCH3	0.0715	-192.3528	-192.3587	0.0058	-192.3528
Anti CH2=C·OCH3	0.0715	-192.3618	-192.3679	0.0061	-192.3618
Anti CH2=CHOC·H2	0.0713	-192.3787	-192.3844	0.0057	-192.3787

[a]Optimized at the B3lyp/6-31G(d,p) level of theory, [b]ZPVE : scaled zero-point energies in kcal/mol, [c] Sum of elec = Sum of electronic and zero-point Energies, [d] Sum of zpe = Sum of electronic and thermal Enthalpies, [e]Therm.corr. : Thermal corrections in Hartree, [f]Unit in Hartree = 627.51 kcal/mol.

Table 2.5 Energy Values, Target Vinyl Alcohols and Ethers

Species	ZPVE[a]	Thermal. corr[b].	Total Energy B3LYP/6-31[c]	B3LYP/6-311[d]	Qcisd(t)[e]	CBS-Q(298) [f]
Anti $CH_2=CHOH$	0.056	0.0048	-153.7522	-153.8142	-153.3172	-153.5560
Anti $C\cdot H=CHOH$	0.042	0.0049	-153.0721	-153.0552	-152.1152	-152.8763
Anti $CH_2=C\cdot OH$	0.043	0.0047	-153.0853	-153.2042	-152.2592	-152.8877
Anti $CH_2=CHOCH_3$	0.084	0.0053	-193.0297	-192.7412	-191.4692	-192.7670
Anti $C\cdot H=CHOCH_3$	0.071	0.0055	-192.3485	-192.0262	-190.8002	-192.0860
Anti $CH_2=C\cdot OCH_3$	0.072	0.0061	-192.3609	-191.6092	-190.3782	-192.0970
Anti $CH_2=CHOC\cdot H_2$	0.070	0.0061	-192.3789	-191.6472	-190.4112	-192.1140
Syn $CH_2=CHOH$	0.057	0.0046	-153.7547	-153.8164	-153.3197	-153.5590
Syn $C\cdot H=CHOH$	0.043	0.0047	-153.0753	-153.1335	-152.1930	-152.8856
Syn $CH_2=C\cdot OH$	0.043	0.0047	-153.0839	-153.1461	-152.2012	-152.8946
Syn $CH_2=CHOCH_3$	0.085	0.0057	-193.0317	-193.0973	-191.8251	-192.7692
Syn $C\cdot H=CHOCH_3$	0.072	0.0058	-192.3528	-192.4175	-191.1917	-192.0962
Syn $CH_2=C\cdot OCH_3$	0.072	0.0061	-192.3618	-192.4312	-191.2001	-192.1038
Syn $CH_2=CHOC\cdot H_2$	0.071	0.0057	-192.3787	-192.4482	-191.2118	-192.1206

[a] ZPVE : scaled zero-point energies in Hartree (scaled by 0.9806) [b] Therm. corr. : Thermal corrections in Hartree. [c] B3lyp/6-31G(d,p). Total energies are in Hartree at 0 K. [d] B3lyp/6-311+G(3df,2p). [e] QCISD(T)/6-31G(d,p). [f] CBS-Q enthalpies are in Hartree, which include thermal correction and zero point energy at 298.15 K.

Table 2.6-a Reaction Enthalpies for Syn Structures

Isodesmic Reaction (Syn structure)	B3LYP /6–31G(d,p)	B3LYP /6–311++G(2fd,2p)	Qcisd(t)[e] /6–31G(d,p)	CBS-Q
$CH_2=CHOH + CH_3CH_3 = CH_3CH_2OH + CH_2=CH_2$	8.69	11.57	3.48	6.09
$CH_2=CHOH + CH_4 = CH_3OH + CH_2=CH_2$	14.62	17.21	6.71	11.88
$CH_2=CHOH + CH_3CH_2CH_3 = CH_3CH_2OH + CH_2=CHCH_3$	5.40	8.43	1.27	3.21
$CH_2=CHOCH_3 + CH_3CH_2CH_3 = CH_3CH_2OCH_3 + CH_2=CHCH_3$	4.31	6.20	1.13	2.92
$CH_2=CHOCH_3 + CH_3CH_3 = CH_3OCH_3 + CH_2=CHCH_3$	7.54	8.99	5.37	6.01
$C\cdot H=CHOH + CH_2=CH_2 = C\cdot H=CH_2 + CH_2=CHOH$	-5.95	-7.73	-2.44	-3.14
$CH_2=C\cdot OH + CH_2=CH_2 = C\cdot H=CH_2 + CH_2=CHOH$	6.67	9.57	0.81	2.57
$CH_2=C\cdot OH + CH_3CH_2OH = CH_3C\cdot HOH + CH_2=CHOH$	-15.34	-18.67	-9.66	-12.92
$C\cdot H=CHOCH_3 + CH_3OCH_3 = C\cdot H_2OCH_3 + CH_2=CHOCH_3$	-21.39	-29.67	-14.37	-17.57
$C\cdot H=CHOCH_3 + CH_2=CH_2 = C\cdot H=CH_2 + CH_2=CHOCH_3$	-3.37	-6.79	-0.67	-2.86
$CH_2=C\cdot OCH_3 + CH_2=CH_2 = C\cdot H=CH_2 + CH_2=CHOCH_3$	4.67	10.60	0.08	1.9
$CH_2=C\cdot OCH_3 + CH_3OCH_3 = C\cdot H_2OCH_3 + CH_2=CHOCH_3$	-19.54	-24.31	-7.51	-12.81
$CH_2=CHOC\cdot H_2 + CH_3OCH_3 = C\cdot H_2OCH_3 + CH_2=CHOCH_3$	-6.49	-8.82	1.07	-2.27

Table 2.6-b Enthalpies of Formation for Syn Structures

Isodesmic Reaction (Syn structure)	B3LYP /6-31G(d,p)	B3LYP /6-311++G(2fd,2p)	Qcisd(t)^e /6-31G(d,p)	CBS-Q
$\mathbf{CH_2{=}CHOH} + CH_3CH_3 = CH_3CH_2OH + CH_2{=}CH_2$	-30.27	-30.86	-29.84	-29.73
$\mathbf{CH_2{=}CHOH} + CH_4 = CH_3OH + CH_2{=}CH_2$	-31.56	-32.13	-29.91	-29.78
$\mathbf{CH_2{=}CHOH} + CH_3CH_2CH_3 = CH_3CH_2OH + CH_2{=}CHCH_3$	-30.16	-30.62	-29.75	-29.62
Average	-30.66± 0.77	-31.2± 0.81	-29.83± 0.08	-29.71 ± 0.15
$\mathbf{CH_2{=}CHOCH_3} + CH_3CH_2CH_3 = CH_3CH_2OCH_3 + CH_2{=}CHCH_3$	-26.83	-27.41	-25.12	-24.83
$\mathbf{CH_2{=}CHOCH_3} + CH_3CH_3 = CH_3OCH_3 + CH_2{=}CHCH_3$	-27.95	-28.26	-25.64	-25.2
Average	-27.39± 0.79	-27.84± 0.60	-25.38± 0.36	-25.02 ± 0.42
$\mathbf{C{\cdot}H{=}CHOH} + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOH$	33.98	34.06	33.65	32.34
$\mathbf{CH_2{=}C{\cdot}OH} + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOH$	30.49	30.91	27.68	26.63
$\mathbf{CH_2{=}C{\cdot}OH} + CH_3CH_2OH = CH_3C{\cdot}HOH + CH_2{=}CHOH$	28.93	29.49	27.15	26.1
Average	29.71± 1.10	30.2± 1.00	27.42± 0.37	26.37 ± 0.63
$\mathbf{C{\cdot}H{=}CHOCH_3} + CH_3OCH_3 = C{\cdot}H_2OCH_3 + CH_2{=}CHOCH_3$	41.68	41.86	38.67	37.14
$\mathbf{C{\cdot}H{=}CHOCH_3} + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOCH_3$	38.77	39.86	37.81	36.75
Average	40.23± 2.05	40.86± 1.41	38.24± 0.60	36.94 ± 0.48
$\mathbf{CH_2{=}C{\cdot}OCH_3} + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOCH_3$	34.97	35.09	33.45	32
$\mathbf{CH_2{=}C{\cdot}OCH_3} + CH_3OCH_3 = C{\cdot}H_2OCH_3 + CH_2{=}CHOCH_3$	35.86	36.09	33.26	32.38
Average	35.42± 0.62	35.59± 0.70	33.36± 0.13	32.19 ± 0.46
$\mathbf{CH_2{=}CHOC{\cdot}H_2} + CH_3OCH_3 = C{\cdot}H_2OCH_3 + CH_2{=}CHOCH_3$	25.13	25.94	23.48	21.84

[a] The reaction enthalpies and $\Delta H_f{}^{\circ}{}_{298}$ are calculated at the CBS-Q//B3LYP/6-31G(d,p) levels.

[b] Deviation : Error bar (±) = Σ STD molecules + STD (standard deviation).

Table 2.7-a Reaction Enthalpies for Anti Structures

Isodesmic Reaction (Anti structure)	B3LYP /6-31G(d,p)	B3LYP/6-311++G(2fd,2p)	Qcisd(t)^e /6-31G(d,p)	CBS-Q
$\mathbf{CH_2{=}CHOH} + CH_3CH_3 = CH_3CH_2OH + CH_2{=}CH_2$	5.57	5.94	3.97	4.34
$\mathbf{CH_2{=}CHOH} + CH_4 = CH_3OH + CH_2{=}CH_2$	12.84	13.67	9.73	10.12
$\mathbf{CH_2{=}CHOH} + CH_3CH_2CH_3 = CH_3CH_2OH + CH_2{=}CHCH_3$	2.51	3.26	0.82	1.46
$\mathbf{CH_2{=}CHOCH_3} + CH_3CH_2CH_3 = CH_3CH_2OCH_3 + CH_2{=}CHCH_3$	3.49	4.91	1.16	1.38
$\mathbf{CH_2{=}CHOCH_3} + CH_3CH_3 = CH_3OCH_3 + CH_2{=}CHCH_3$	5.96	6.79	3.40	4.48
$\mathbf{C{\cdot}H{=}CHOH} + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOH$	-9.61	-10.63	-7.72	-8.3
$\mathbf{CH_2{=}C{\cdot}OH} + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOH$	-5.73	-8.16	-0.87	-1.14
$\mathbf{CH_2{=}C{\cdot}OH} + CH_3CH_2OH = CH_3C{\cdot}HOH + CH_2{=}CHOH$	-23.84	-24.66	-15.46	-17.27
$\mathbf{C{\cdot}H{=}CHOCH_3} + CH_3OCH_3 = C{\cdot}H_2OCH_3 + CH_2{=}CHOCH_3$	-26.77	-28.23	-20.21	-22.62
$\mathbf{C{\cdot}H{=}CHOCH_3} + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOCH_3$	-10.22	-13.49	-4.31	-7.91
$\mathbf{CH_2{=}C{\cdot}OCH_3} + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOCH_3$	-3.45	-5.57	1.06	-0.9
$\mathbf{CH_2{=}C{\cdot}OCH_3} + CH_3OCH_3 = C{\cdot}H_2OCH_3 + CH_2{=}CHOCH_3$	-17.36	-20.18	-13.67	-15.6
$\mathbf{CH_2{=}CHOC{\cdot}H_2} + CH_3OCH_3 = C{\cdot}H_2OCH_3 + CH_2{=}CHOCH_3$	-8.79	-11.57	-1.09	-5.17

Table 2.7-b Enthalpies of Formation for Anti Structures

Isodesmic Reaction (Anti structure)	B3LYP /6–31G(d,p)	B3LYP/6-311++G(2fd,2p)	Qcisd(t)^e /6–31G(d,p)	CBS-Q
$CH_2{=}CHOH + CH_3CH_3 = CH_3CH_2OH + CH_2{=}CH_2$	-28.33	-28.92	-27.9	-27.98
$CH_2{=}CHOH + CH_4 = CH_3OH + CH_2{=}CH_2$	-29.62	-30.19	-27.97	-28.02
$CH_2{=}CHOH + CH_3CH_2CH_3 = CH_3CH_2OH + CH_2{=}CHCH_3$	-28.22	-28.68	-27.81	-27.87
Average	-28.72± 0.77	-29.26± 0.81	-27.89± 0.08	-27.96 ± 0.14
$CH_2{=}CHOCH_3 + CH_3CH_2CH_3 = CH_3CH_2OCH_3 + CH_2{=}CHCH_3$	-24.3	-24.88	-22.59	-23.3
$CH_2{=}CHOCH_3 + CH_3CH_3 = CH_3OCH_3 + CH_2{=}CHCH_3$	-25.42	-25.73	-23.11	-23.67
Average	-24.86± 0.73	-25.31± 0.63	-22.85± 0.39	-23.48 ± 0.45
$C{\cdot}H{=}CHOH + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOH$	36.62	36.7	36.29	37.51
$CH_2{=}C{\cdot}OH + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOH$	34.99	35.41	32.18	30.35
$CH_2{=}C{\cdot}OH + CH_3CH_2OH = CH_3C{\cdot}HOH + CH_2{=}CHOH$	33.43	33.99	31.65	30.46
Average	34.21± 0.96	34.7± 0.69	31.92± 0.39	30.40 ± 0.14
$C{\cdot}H{=}CHOCH_3 + CH_3OCH_3 = C{\cdot}H_2OCH_3 + CH_2{=}CHOCH_3$	47.96	48.14	44.95	43.73
$C{\cdot}H{=}CHOCH_3 + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOCH_3$	45.05	46.14	44.09	43.34
Average	46.51± 0.47	47.14± 0.53	44.52± 0.37	43.54 ± 0.47
$CH_2{=}C{\cdot}OCH_3 + CH_2{=}CH_2 = C{\cdot}H{=}CH_2 + CH_2{=}CHOCH_3$	39.67	39.79	38.15	36.33
$CH_2{=}C{\cdot}OCH_3 + CH_3OCH_3 = C{\cdot}H_2OCH_3 + CH_2{=}CHOCH_3$	40.56	40.79	37.96	36.71
Average	40.12± 0.61	40.29± 0.79	38.06± 0.72	36.52 ± 0.46
$CH_2{=}CHOC{\cdot}H_2 + CH_3OCH_3 = C{\cdot}H_2OCH_3 + CH_2{=}CHOCH_3$	30.92	31.73	29.27	26.28

[a] The reaction enthalpies and $\Delta H_f^o{}_{298}$ are calculated at the CBS-Q//B3LYP/6-31G(d,p) levels.

[b] Deviation : Error bar (±) = Σ STD molecules + STD (standard deviation).

2.4.3 Rotational Barriers

Potential energy diagrams for internal rotations in each molecule are calculated at the B3LYP/6-31g(d,p) density functional level. Data are presented in Appendix Table2.8 through 2.18. The potential energy as function of dihedral angle is determined by scanning the torsion angles from 0 to 360 at 15 intervals allowing the remaining molecular structural parameters to be optimized. The barriers for internal rotations are calculated from the maximum in the barrier and minimum of conformer as a function of torsional angle. Diagrams of potential energy vs. torsion angle for internal rotations about the carbon - oxygen bonds of the molecules are shown in Figures 2.8 through 2.18.

The values of the coefficients of the Fourier expansion, a_i and b_i in equation are listed in Table 2.8. The values of the coefficients a_i and b_i are calculated to provide the minima and maxima of the torsional potentials with allowance of a shift of the theoretical extreme angular positions. Rotations about the CH_2=CH---OH bond of CH_2=CHOH show potentials consisting of one minima and two maxima. The density functional calculated rotational barrier for CH_2=CHOH is 5.76 kcal/mol is shown in Figure 8. The H-H syn conformer is the most stable (0° dihedral). The H-H eclipsed structure with energy of 2.05 kcal/mol is more stable than the H-H anti clinal structure, which has the highest energy, 5.76 kcal/mol.

Table 2.8 Coefficients (kcal/mol)[a] of Truncated Fourier Series Representation for Internal Rotation Potentials

Rotors	a_0	a_1	a_2	a_3	a_4	a_5	b_1	b_2	b_3	b_4	b_5
CH_2=CH---OH	3.312	0.640	-2.364	0.392	0.079	-0.004	0.012	-0.082	0.020	0.005	0.000
C·H=CH---OH	3.117	0.863	-1.968	0.366	0.060	-0.014	-0.001	0.002	-0.001	0.000	0.000
CH_2=C·---OH	1.319	-0.716	-0.013	-0.225	-0.274	-0.009	0.881	-0.076	-0.120	0.118	0.041
CH_2=CHO---CH_3	0.457	-0.002	0.015	-0.515	-0.007	0.007	0.000	-0.001	0.033	0.000	0.000
CH_2=CH---OCH_3	3.520	0.200	-2.453	0.937	0.004	-0.015	-0.006	0.130	-0.075	0.001	0.003
C·H=CHO---CH_3	0.464	0.002	0.020	-0.562	-0.003	0.011	0.002	-0.003	0.003	0.002	-0.003
C·H=CH---OCH_3	3.523	0.556	-2.079	0.951	0.006	-0.024	0.000	0.001	0.000	0.000	0.000
CH_2=C·O---CH_3	0.512	-0.001	0.010	-0.511	-0.011	0.001	-0.003	0.001	-0.021	0.000	-0.001
CH_2=C·---OCH_3	1.066	-0.198	-0.127	-0.385	0.086	0.050	0.656	-0.085	0.319	0.202	-0.005
CH_2=CHO---C·H_2	1.870	0.075	2.381	0.209	0.695	0.144	-0.372	0.625	-0.475	0.403	-0.132
CH_2=CH---OC·H_2	2.159	0.095	-2.257	0.192	0.285	-0.138	0.000	0.072	-0.009	-0.017	0.009

[a] Unit in kcal/mol. Values of rotational barriers computed using the B3lyp/6-31G(d,p) theory. Coefficients are calculated as follows: $V(\varnothing) = a_0 + a_1\cos(\varnothing) + a_2\cos(\varnothing) + a_3\cos(\varnothing) + a_4\cos(\varnothing) + a_5\cos(\varnothing) + b_1\sin(\varnothing) + b_2\sin(\varnothing) + b_3\sin(\varnothing) + b_4\sin(\varnothing) + b_5\sin(\varnothing)$.

Figure 2.9 shows the calculated C·H=CH---OH rotational barriers in C·H=CHOH. The H-H eclipsed structure has highest energy, 5.13 kcal/mol at 90.3 angle. The H-H eclipsed structure has lowest energy at the 0 angle.

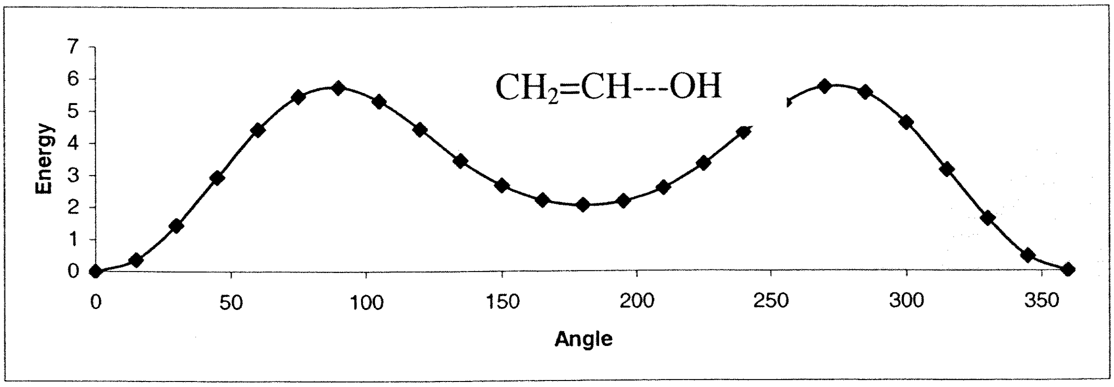


Figure 2.8 Internal Rotation Barriers CH_2=CH---OH

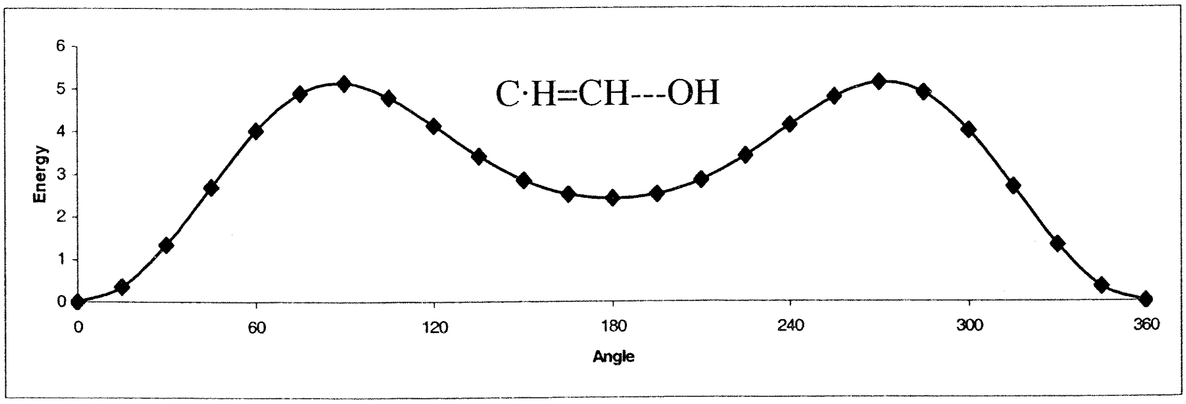


Figure 2.9 Internal Rotation Barriers C·H=CH---OH

Figures 2.11 through 2.12 illustrate the potential barrier for two rotations in methyl vinyl ether. Figures 2.13 through 2.18 show the rotational barriers for the methyl vinyl ether and the radical species resulting from loss of a hydrogen atom from the vinyl alcohol and methyl vinyl ether.

The CH_2 = CH---O---CH_3 rotor in methyl vinyl ether and in the corresponding radicals (C·H=$CHOCH_3$, CH_2=C·OCH_3) show a uniform, symmetric 3 fold barrier with height near 1 kcal/mole. The CH_2=CHOC·H_2 (methylene radical rotor) shows two fold barrier with height corresponding to about 5 kcal/mole, which results from stabilization (overlap) between the radical and the oxygen orbitals.

The vinyl--OH, vinyl--OCH_3, the corresponding radicals (C·H=CH--OH and C·H=CHO--CH_3), and the Vinyl--OC·H_2 radical (all carbon-double bond--oxygen rotation) show two fold barrier with height about 5-6 kcal/mole. The Vinyl radicals where the radical site is on the carbon of the oxygen bond (CH_2=C·OH and CH_2=C·OCH_3) both show a two fold barrier, but with barrier heights only 2 kcal/mole.

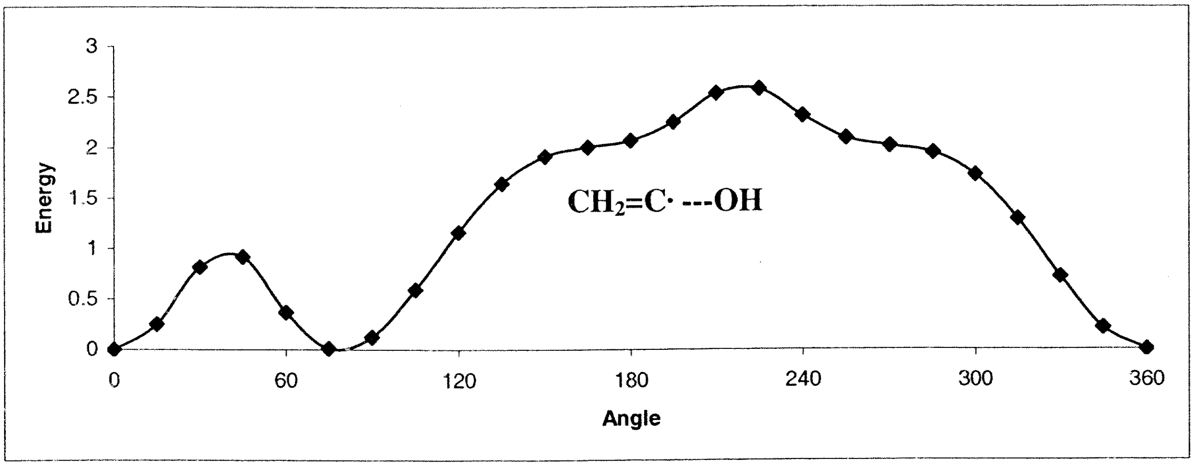


Figure 2.10 Internal Rotation Barriers CH_2=C· ---OH

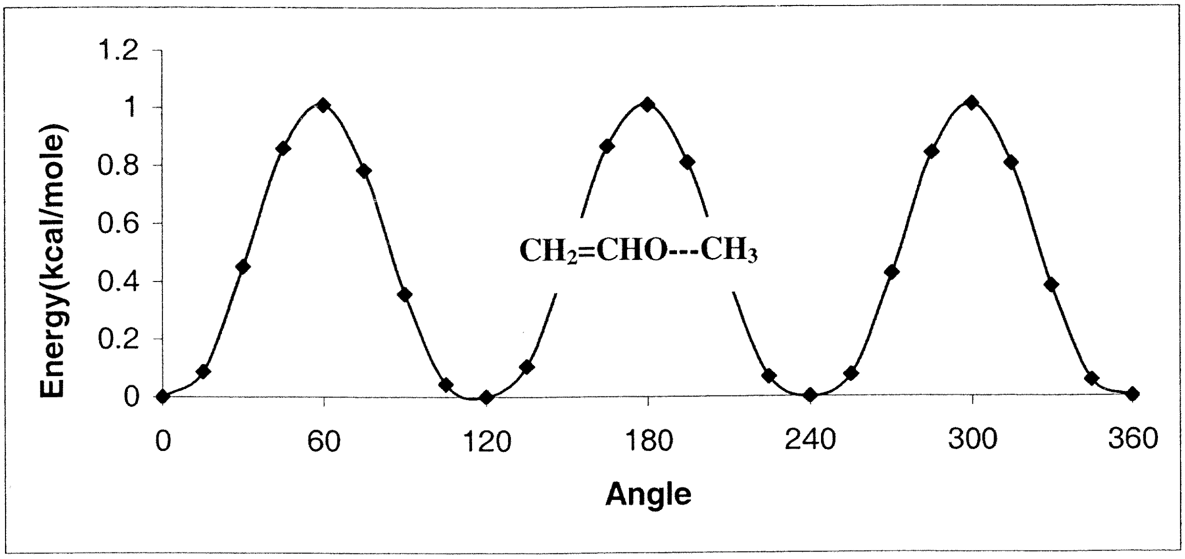


Figure 2.11 Internal Rotation Barriers CH_2=CHO---CH_3

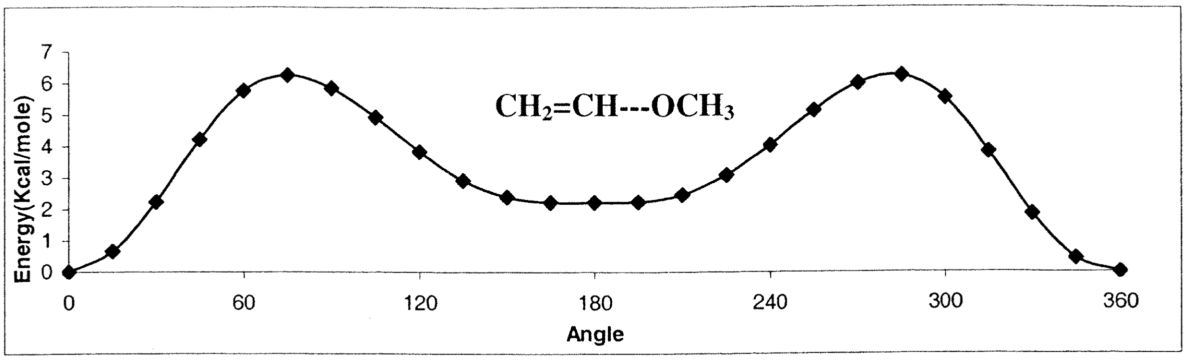


Figure 2.12 Internal Rotation Barriers CH_2=CH---OCH_3

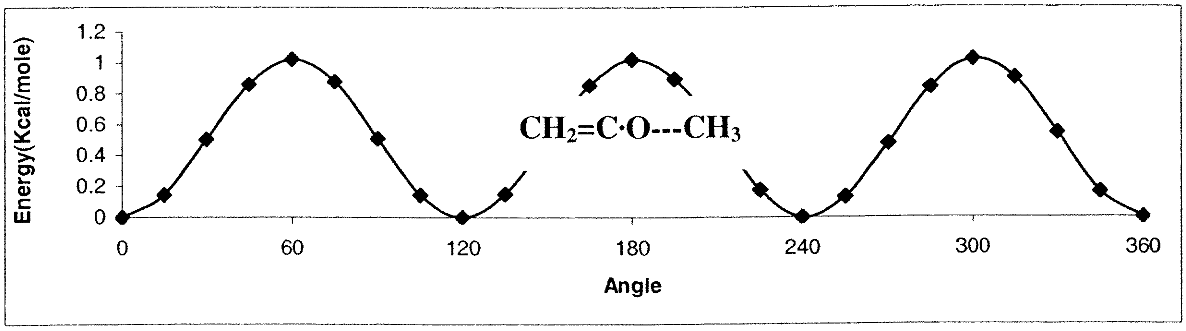


Figure 2.13 Internal Rotation Barriers CH_2=C·O---CH_3

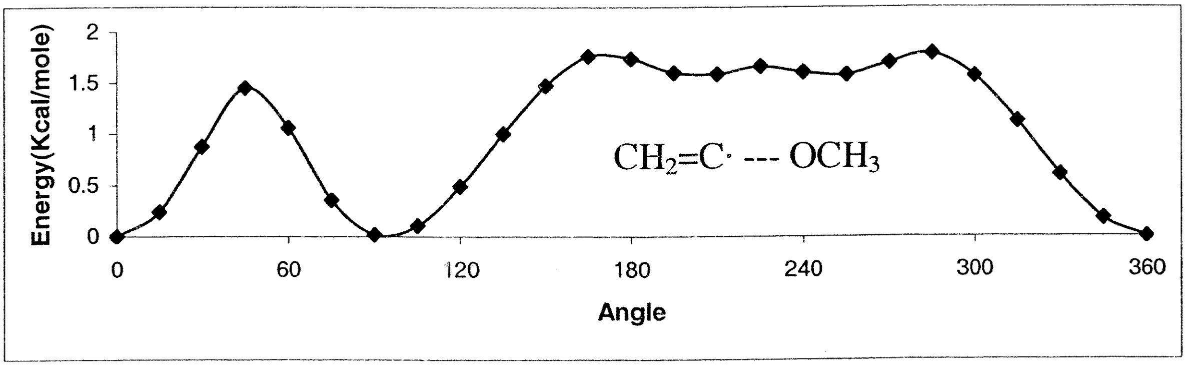


Figure 2.14 Internal Rotation Barriers CH_2=C· --- OCH_3

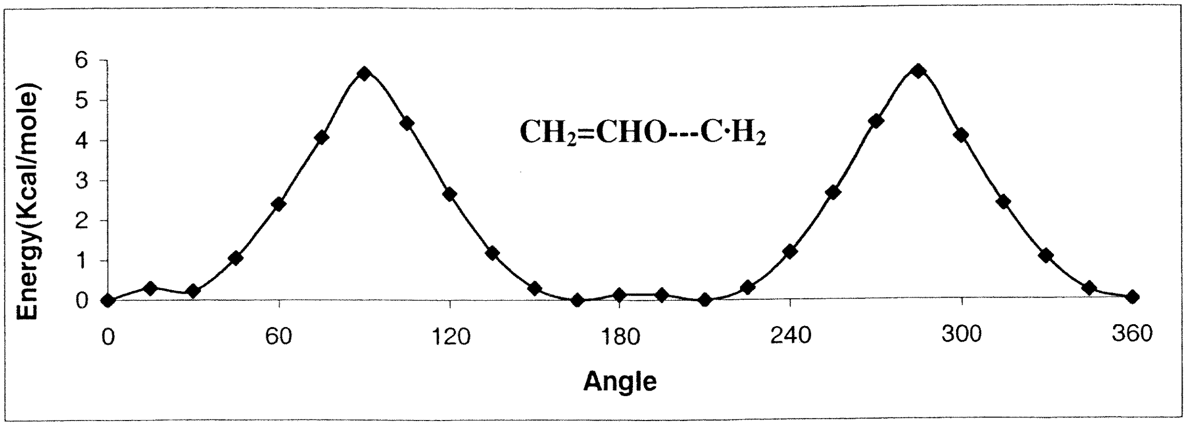


Figure 2.15 Internal Rotation Barriers CH_2=CHO---C·H_2

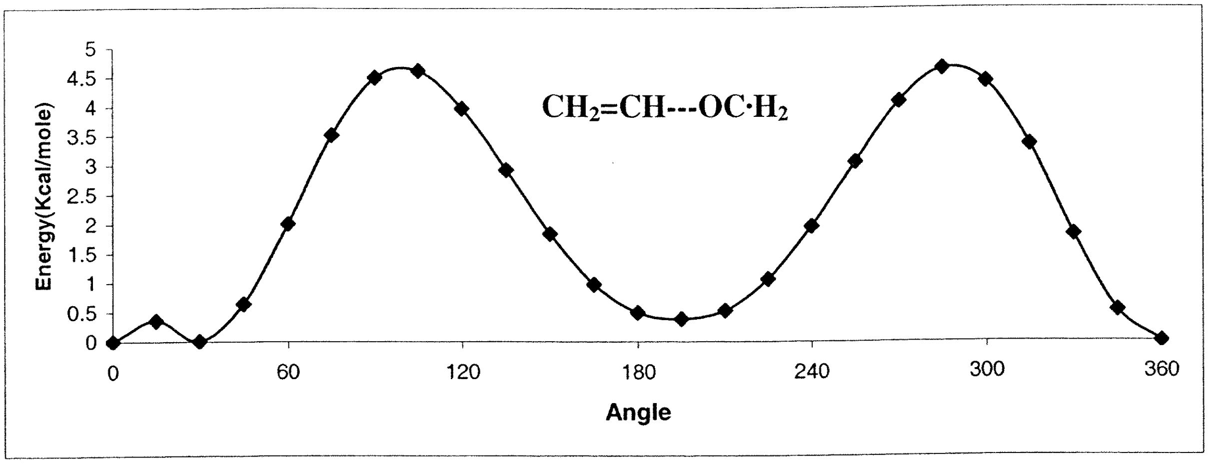


Figure 2.16 Internal Rotation Barriers CH_2=CH---OC·H_2

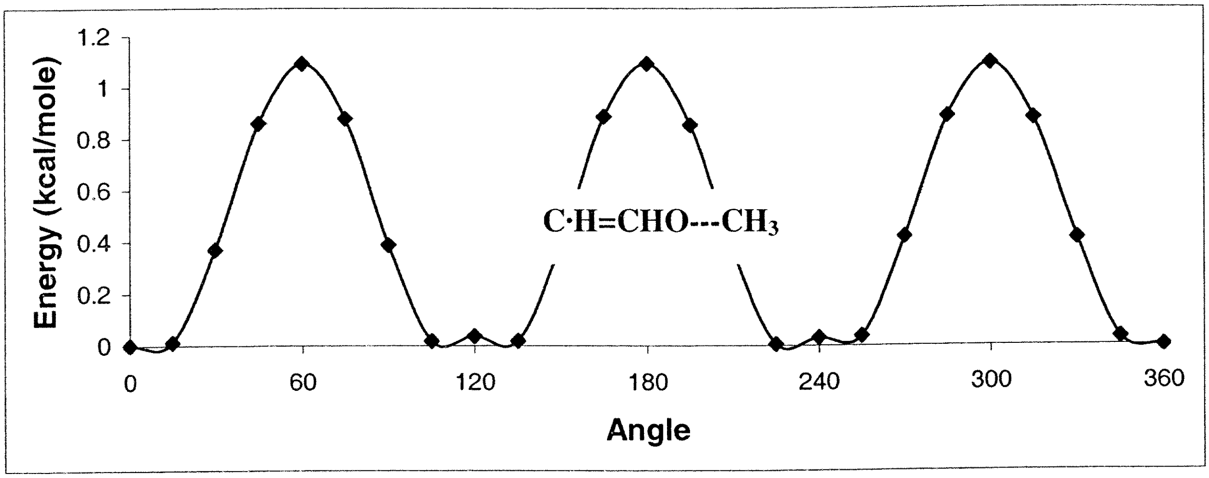


Figure 2.17 Internal Rotation Barriers C·H=CHO---CH_3

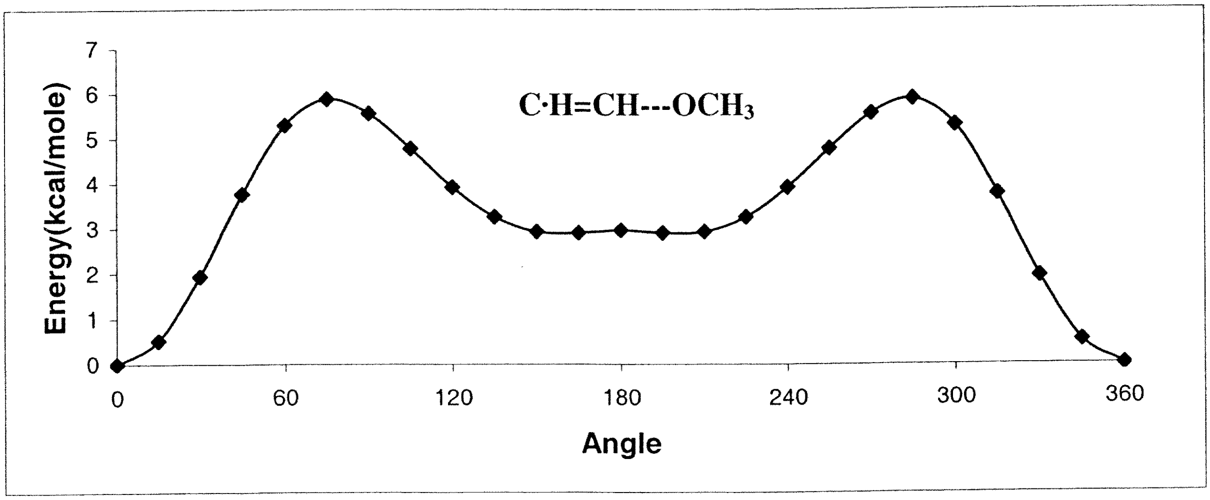


Figure 2.18 Internal Rotation Barriers C·H=CH---OCH_3

2.4.4 Entropy, S°_{298} and Heat Capacity, $C_p(T)$ from 10 to 5000 K

The entropy and heat capacity results using B3LYP/6-31g(d,p) determined geometries and frequencies are summarized in Tables 2.9 through 2.12. TVR represents the sum of the contributions from translations, vibrations and external rotations (TVR) for S°_{298} and $C_p(T)$'s. The torsion frequencies for the internal rotors are not included in TVR. Instead, more accurate contribution from hindered rotations is calculated for the contributions to S°_{298} and $C_p(T)$'s from the internal rotation (IR) about $CH_2 = CH$---OH bonds for vinyl alcohols and $CH_2 = CH$---O---CH_3 bonds for methyl vinyl ethers and corresponding radicals. The final standard entropies also include correction terms for rotational conformers. This correction is calculated by the following formula for 1 mole of mixture.[31]:

$$\Delta S_{\text{mixing}} = -R\Sigma n_i \ln(n_i)$$

where n_i is the equilibrium mole fraction of the ith form. ΔS_{mixing} represents the entropy of mixing of rotational conformations or optical conformations.

Table 2.9 $\Delta H_f°_{(298)}$, Entropy and Heat Capacities of methyl vinyl ether[a] and radicals ($CH_2=CHOCH_3$, $C{\cdot}H=CHOCH_3$, $CH_2=C{\cdot}OCH_3$, and $CH_2=CHOC{\cdot}H_2$)

Species		$\Delta H°_{298}$[b]	S[c]	C_p[c]: 300	400	500	600	800	1000	1500
Anti $CH_2=CHOCH_3$	TVR[d]		62.41	14.56	18.83	22.85	26.33	31.87	36.00	42.47
	I.R1[e]		5.42	1.50	1.32	1.22	1.16	1.09	1.06	1.02
	I.R2[e]		3.63	3.48	3.77	3.63	3.34	2.71	2.19	1.36
	Total[f]	-23.48±0.45	71.46	19.53	23.93	27.70	30.83	35.67	39.25	44.86
Syn $CH_2=CHOCH_3$	TVR[d]		62.46	14.27	18.41	22.23	25.50	30.70	34.65	41.14
	I.R1[e]		5.42	1.50	1.32	1.22	1.16	1.09	1.06	1.02
	I.R2[e]		3.63	3.48	3.77	3.63	3.34	2.71	2.19	1.36
	Total[f]	-25.02±0.42	71.51	19.25	23.50	27.08	30.00	34.50	37.90	43.52
Anti $C{\cdot}H=CHOCH_3$	TVR[d]		65.92	14.31	17.32	19.71	21.49	23.78	25.06	26.51
	I.R1[e]		5.36	1.57	1.37	1.26	1.19	1.11	1.07	1.03
	I.R2[e]		3.36	3.11	3.80	3.93	3.71	2.98	2.36	1.42
	Total[f]	43.54±0.47	74.65	18.99	22.49	24.90	26.39	27.87	28.48	28.95
Syn $C{\cdot}H=CHOCH_3$	TVR[d]		64.05	14.50	18.25	21.68	24.62	29.24	32.68	38.05
	I.R1[e]		5.36	1.57	1.37	1.26	1.19	1.11	1.07	1.03
	I.R2[e]		3.36	3.11	3.80	3.93	3.71	2.98	2.36	1.42
	Total[f]	36.94±0.48	72.77	19.18	23.42	26.87	29.52	33.33	36.11	40.50
Anti $CH_2=C{\cdot}OCH_3$	TVR[d]		63.70	14.28	17.96	21.38	24.34	29.03	32.53	37.98
	I.R1[e]		5.44	1.50	1.32	1.22	1.16	1.09	1.06	1.02
	I.R2[e]		5.96	2.57	2.12	1.79	1.57	1.31	1.16	0.88
	Total[f]	36.52±0.46	75.10	18.34	21.40	24.39	27.07	31.43	34.74	39.88
Syn $CH_2=C{\cdot}OCH_3$	TVR[d]		64.36	14.60	18.28	21.66	24.58	29.19	32.64	38.04
	I.R1[e]		5.44	1.50	1.32	1.22	1.16	1.09	1.06	1.02
	I.R2[e]		5.96	2.57	2.12	1.79	1.57	1.31	1.16	0.88
	Total[f]	32.19±0.46	75.76	18.67	21.72	24.67	27.31	31.59	34.86	39.94
Anti $CH_2=CHOC{\cdot}H_2$	TVR[d]		65.99	15.15	19.05	22.45	25.29	29.68	32.93	38.11
	I.R1[e]		4.03	1.48	1.56	1.62	1.66	1.64	1.58	1.40
	I.R2[e]		5.31	2.13	2.13	2.11	2.05	1.86	1.64	1.18
	Total[f]	26.28	75.33	18.75	22.74	26.18	28.99	33.18	36.16	40.69
Syn $CH_2=CHOC{\cdot}H_2$	TVR[d]		65.94	14.80	18.79	22.27	25.16	29.60	32.87	38.07
	I.R1[e]		4.03	1.48	1.56	1.62	1.66	1.64	1.58	1.40
	I.R2[e]		5.31	2.13	2.13	2.11	2.05	1.86	1.64	1.18
	Total[f]	21.84	75.28	18.41	22.48	26.00	28.87	33.10	36.09	40.65

[a] Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm.
[b] Units in kcal/mol. [c] Units in cal/(mol k). [d] The sum of contributions from translations, external rotations, and vibrations. [e] Contribution from internal rotation about the $CH_2=CHO{-}{-}{-}CH_3$ and $CH_2=CH{-}{-}{-}OCH_3$. [f] Total = TVR + I.R1 + I.R2.

Table 2.10 $\Delta H_f°_{(298)}$,, Entropy and Heat Capacities of Vinyl Alcohol[a] (CH_2=CHOH, C·H=CHOH, CH_2=C·OH)

Species		$\Delta H°_{298}$[b]	S[c]	C_p[c]: 300	400	500	600	800	1000	1500
Anti CH_2=CHOH	TVR[d]		60.28	12.14	15.02	17.59	19.73	23.04	25.51	29.52
	I.R1[e]		1.45	2.68	3.12	3.16	3.01	2.57	2.19	1.62
	Total[f]	-27.96±0.14	61.73	14.82	18.15	20.75	22.74	25.61	27.69	31.15
Syn CH_2=CHOH	TVR[d]		61.68	12.11	15.00	17.56	19.71	23.03	25.51	29.53
	I.R1[e]		1.45	2.68	3.12	3.16	3.01	2.57	2.19	1.62
	Total[f]	-29.71±0.15	63.13	14.79	18.12	20.72	22.72	25.60	27.70	31.15
Anti C·H=CHOH	TVR[d]		61.62	12.19	14.50	16.44	18.02	20.42	22.20	25.13
	I.R1[e]		1.42	2.63	3.23	3.33	3.15	2.61	2.16	1.56
	Total[f]	37.51	63.04	14.83	17.73	19.77	21.17	23.03	24.37	26.69
Syn C·H=CHOH	TVR[d]		61.66	12.20	14.51	16.45	18.03	20.43	22.20	25.13
	I.R1[e]		1.42	2.63	3.23	3.33	3.15	2.61	2.16	1.56
	Total[f]	32.34	63.08	14.83	17.74	19.78	21.18	23.04	24.36	26.69
Anti CH_2=C·OH	TVR[d]		61.23	11.95	14.22	16.18	17.79	20.26	22.10	25.10
	I.R1[e]		3.27	2.14	2.07	1.89	1.72	1.47	1.32	1.15
	Total[f]	30.40±0.14	64.50	14.08	16.29	18.06	19.50	21.73	23.42	26.25
Syn CH_2=C·OH	TVR[d]		62.13	12.91	15.03	16.84	18.34	20.65	22.38	25.24
	I.R1[e]		3.27	2.14	2.07	1.89	1.72	1.47	1.32	1.15
	Total[f]	26.37±0.63	65.40	15.05	17.10	18.73	20.06	22.12	23.70	26.39

[a] Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm). [b] Units in kcal/mol. [c] Units in cal/(mol k). [d] The sum of contributions from translations, external rotations, and vibrations. [e] Contribution from internal rotation about the CH_2=CH---OH. [f] Total = TVR + I.R1 + I.R2.

Table 2.11a Heat Capacities of Vinyl Alcohol and Corresponding Radicals[a]

	Anti CH_2=CHOH			Syn CH_2=CHOH			Anti C·H=CHOH		
Cp	TVR	I.R1	Total	TVR	I.R1	Total	TVR	I.R1	Total
10	7.95	0	7.95	7.95	0	7.95	7.95	0	7.95
20	7.95	0	7.95	7.95	0	7.95	7.95	0	7.95
25	7.95	0	7.95	7.95	0	7.95	7.95	0	7.95
50	7.95	0	7.95	7.95	0	7.95	7.95	0	7.95
100	8.04	0.23	8.27	8.05	0.23	8.28	8.11	0.27	8.38
150	8.53	0.85	9.38	8.55	0.85	9.4	8.77	0.85	9.62
200	9.46	0.59	10.04	9.48	0.59	10.06	9.8	0.49	10.29
250	10.7	0.22	10.92	10.72	0.22	10.94	10.98	0.11	11.09
300	12.14	2.68	14.82	12.11	2.68	14.79	12.19	2.63	14.83
400	15.02	3.12	18.15	15	3.12	18.12	14.5	3.23	17.73
500	17.59	3.16	20.75	17.56	3.16	20.72	16.44	3.33	19.77
600	19.73	3.01	22.74	19.71	3.01	22.72	18.02	3.15	21.17
800	23.04	2.57	25.61	23.03	2.57	25.6	20.42	2.61	23.03
1000	25.51	2.19	27.69	25.51	2.19	27.69	22.2	2.16	24.36
1500	29.52	1.62	31.14	29.53	1.62	31.16	25.13	1.56	26.69
2000	31.72	1.37	33.09	31.73	1.37	33.1	26.76	1.32	28.07
2500	32.98	1.24	34.22	32.99	1.24	34.23	27.7	1.2	28.9
3000	33.75	1.17	34.91	33.76	1.17	34.92	28.28	1.14	29.41
3500	34.24	1.12	35.36	34.25	1.12	35.37	28.65	1.1	29.75
4000	34.58	1.09	35.67	34.59	1.09	35.68	28.91	1.07	29.98
4500	34.82	1.07	35.89	34.82	1.07	35.89	29.09	1.06	30.14
5000	34.99	1.06	36.05	35	1.06	36.05	29.22	1.04	30.26

Table 2.11-b Heat Capacities of Vinyl Alcohol and Corresponding Radicals[a]

	Syn C·H=CHOH			Anti CH_2=C·OH			Syn CH_2=C·OH		
Cp	TVR	I.R1	Total	TVR	I.R1	Total	TVR	I.R1	Total
10	7.95	0	7.95	7.95	0.76	8.71	7.95	0.76	8.71
20	7.95	0	7.95	7.95	0.72	8.67	7.95	0.72	8.67
25	7.95	0	7.95	7.95	0.56	8.51	7.95	0.56	8.51
50	7.95	0	7.95	7.95	0.27	8.22	7.95	0.27	8.22
100	8.12	0.27	8.39	8.12	0.75	8.87	8.11	0.75	8.86
150	8.79	0.85	9.63	8.76	0.35	9.11	8.72	0.35	9.07
200	9.8	0.49	10.29	9.73	0.79	10.52	9.66	0.79	10.45
250	10.97	0.11	11.08	10.87	0.04	10.91	10.77	0.04	10.81
300	12.2	2.63	14.83	11.95	2.14	14.08	12.91	2.14	15.05
400	14.51	3.23	17.74	14.22	2.07	16.29	15.03	2.07	17.1
500	16.45	3.33	19.78	16.18	1.89	18.06	16.84	1.89	18.73
600	18.03	3.15	21.18	17.79	1.72	19.5	18.34	1.72	20.06
800	20.43	2.61	23.04	20.26	1.47	21.73	20.65	1.47	22.11
1000	22.2	2.16	24.37	22.1	1.32	23.42	22.38	1.32	23.7
1500	25.13	1.56	26.69	25.1	1.15	26.25	25.24	1.15	26.39
2000	26.76	1.32	28.07	26.75	1.08	27.84	26.83	1.08	27.91
2500	27.7	1.2	28.9	27.7	1.05	28.75	27.75	1.05	28.8
3000	28.28	1.14	29.41	28.28	1.03	29.31	28.32	1.03	29.35
3500	28.65	1.1	29.75	28.66	1.02	29.68	28.68	1.02	29.7
4000	28.91	1.07	29.98	28.91	1.02	29.93	28.93	1.02	29.95
4500	29.09	1.06	30.14	29.09	1.01	30.1	29.11	1.01	30.12
5000	29.22	1.04	30.26	29.22	1.01	30.23	29.23	1.01	30.24

[a] Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm.

Table 2.12-a Heat Capacities of Methyl Vinyl Ethers and Radicals [a]

	Anti $CH_2=CHOCH_3$				Syn $CH_2=CHOCH_3$				Anti $C{\cdot}H=CHOCH_3$				Syn $C{\cdot}H=CHOCH_3$			
Cp	TVR	I.R1	I.R2	Total	TVR	I.R1	I.R2	Total	TVR	I.R1	I.R2	Total	TVR	I.R1	I.R2	Total
10	7.95	0.21	0	8.16	7.95	0.21	0	8.16	7.95	0.65	0	8.6	7.95	0.65	0	8.6
20	7.95	0.09	0.02	8.06	7.95	0.09	0.02	8.06	7.95	0.31	0.02	8.27	7.95	0.31	0.02	8.27
25	7.95	0.14	0.08	8.16	7.95	0.14	0.08	8.16	7.95	0.28	0.07	8.3	7.95	0.28	0.07	8.3
50	7.97	0.86	0.75	9.58	7.97	0.86	0.75	9.58	7.98	0.83	0.74	9.54	7.97	0.83	0.74	9.53
100	8.41	0.83	0.56	9.8	8.48	0.83	0.56	9.87	8.56	0.8	0.55	9.91	8.53	0.8	0.55	9.87
150	9.31	0.94	0.98	11.24	9.48	0.94	0.98	11.41	9.64	0.98	0.85	11.48	9.67	0.98	0.85	11.51
200	10.61	0.8	0.51	11.92	10.84	0.8	0.51	12.16	11.04	0.87	0.17	12.08	11.1	0.87	0.17	12.14
250	12.31	0.64	0.06	13.01	12.56	0.64	0.06	13.26	12.68	0.71	0.62	14.02	12.68	0.71	0.62	14.02
300	14.56	1.5	3.48	19.53	14.27	1.5	3.48	19.25	14.31	1.57	3.11	18.99	14.5	1.57	3.11	19.18
400	18.83	1.32	3.77	23.93	18.41	1.32	3.77	23.5	17.32	1.37	3.8	22.49	18.25	1.37	3.8	23.42
500	22.85	1.22	3.63	27.7	22.23	1.22	3.63	27.08	19.71	1.26	3.93	24.9	21.68	1.26	3.93	26.87
600	26.33	1.16	3.34	30.83	25.5	1.16	3.34	30	21.49	1.19	3.71	26.39	24.62	1.19	3.71	29.52
800	31.87	1.09	2.71	35.67	30.7	1.09	2.71	34.5	23.78	1.11	2.98	27.87	29.24	1.11	2.98	33.33
1000	36	1.06	2.19	39.25	34.65	1.06	2.19	37.9	25.06	1.07	2.36	28.48	32.68	1.07	2.36	36.1
1500	42.47	1.02	1.36	44.86	41.14	1.02	1.36	43.52	26.51	1.03	1.42	28.95	38.05	1.03	1.42	40.5
2000	45.83	1.01	0.91	47.75	44.74	1.01	0.91	46.66	27.07	1.01	0.94	29.02	40.84	1.01	0.94	42.8
2500	47.7	1	0.65	49.34	46.84	1	0.65	48.49	27.33	1	0.67	29	42.39	1	0.67	44.06
3000	48.81	0.98	0.48	50.27	48.15	0.98	0.48	49.6	27.48	0.98	0.5	28.96	43.32	0.98	0.5	44.8
3500	49.52	0.95	0.37	50.84	49	0.95	0.37	50.32	27.57	0.95	0.39	28.91	43.92	0.95	0.39	45.25
4000	50	0.91	0.29	51.2	49.58	0.91	0.29	50.78	27.63	0.91	0.31	28.85	44.32	0.91	0.31	45.54
4500	50.34	0.87	0.24	51.44	49.99	0.87	0.24	51.1	27.67	0.87	0.25	28.79	44.6	0.87	0.25	45.72
5000	50.58	0.82	0.19	51.6	50.3	0.82	0.19	51.31	27.7	0.82	0.21	28.73	44.8	0.82	0.21	45.83

Table 2.12-b Heat Capacities of Methyl Vinyl Ethers and Radicals [a]

	Anti $CH_2=C{\cdot}OCH_3$				Syn $CH_2=C{\cdot}OCH_3$				Anti $CH_2=CHOC{\cdot}H_2$				Syn $CH_2=CHOC{\cdot}H_2$			
Cp	TVR	I.R1	I.R2	Total	TVR	I.R1	I.R2	Total	TVR	I.R1	I.R2	Total	TVR	I.R1	I.R2	Total
10	7.95	0.01	0.01	7.97	7.95	0.01	0.01	7.97	7.95	0.06	0.02	8.03	7.95	0.06	0.02	8.03
20	7.95	0.03	0.14	8.12	7.95	0.03	0.14	8.12	7.95	0.86	0.47	9.28	7.95	0.86	0.47	9.28
25	7.95	0.1	0.32	8.37	7.95	0.1	0.32	8.37	7.95	0.24	0.82	9.01	7.95	0.24	0.82	9.01
50	8.02	0.87	0.24	9.13	7.97	0.87	0.24	9.08	7.96	0.52	0.08	8.56	7.97	0.52	0.08	8.57
100	8.77	0.84	0.06	9.66	8.49	0.84	0.06	9.39	8.32	0.35	0.37	9.04	8.47	0.35	0.37	9.19
150	9.83	0.94	0.6	11.37	9.56	0.94	0.6	11.1	9.33	0.35	0.24	9.93	9.65	0.35	0.24	10.24
200	11.19	0.79	0.83	12.82	10.91	0.79	0.83	12.54	10.88	0.39	0.16	11.43	11.27	0.39	0.16	11.83
250	12.81	0.63	0.77	14.21	12.51	0.63	0.77	13.9	12.76	0.44	0.13	13.32	13.15	0.44	0.13	13.72
300	14.28	1.5	2.57	18.34	14.6	1.5	2.57	18.67	15.15	1.48	2.13	18.75	14.8	1.48	2.13	18.41
400	17.96	1.32	2.12	21.4	18.28	1.32	2.12	21.72	19.05	1.56	2.13	22.74	18.79	1.56	2.13	22.48
500	21.38	1.22	1.79	24.39	21.66	1.22	1.79	24.67	22.45	1.62	2.11	26.18	22.27	1.62	2.11	26
600	24.34	1.16	1.57	27.07	24.58	1.16	1.57	27.31	25.29	1.66	2.05	28.99	25.16	1.66	2.05	28.87
800	29.03	1.09	1.31	31.43	29.19	1.09	1.31	31.6	29.68	1.64	1.86	33.18	29.6	1.64	1.86	33.1
1000	32.53	1.06	1.15	34.74	32.64	1.06	1.15	34.85	32.93	1.58	1.64	36.16	32.87	1.58	1.64	36.1
1500	37.98	1.02	0.87	39.88	38.04	1.02	0.87	39.94	38.11	1.4	1.18	40.69	38.07	1.4	1.18	40.66
2000	40.81	1.01	0.66	42.48	40.84	1.01	0.66	42.51	40.85	1.27	0.86	42.98	40.82	1.27	0.86	42.96
2500	42.37	1	0.51	43.88	42.39	1	0.51	43.9	42.39	1.2	0.64	44.22	42.37	1.2	0.64	44.21
3000	43.31	0.98	0.4	44.68	43.32	0.98	0.4	44.7	43.31	1.14	0.49	44.95	43.3	1.14	0.49	44.94
3500	43.91	0.95	0.32	45.17	43.92	0.95	0.32	45.18	43.91	1.11	0.39	45.4	43.9	1.11	0.39	45.39
4000	44.31	0.91	0.26	45.47	44.32	0.91	0.26	45.48	44.31	1.08	0.31	45.7	44.3	1.08	0.31	45.69
4500	44.59	0.86	0.21	45.67	44.6	0.86	0.21	45.67	44.59	1.05	0.26	45.9	44.58	1.05	0.26	45.89
5000	44.8	0.81	0.18	45.79	44.8	0.81	0.18	45.79	44.8	1.03	0.21	46.04	44.79	1.03	0.21	46.03

[a] Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm.

2.4.5 Bond Energies

The bond dissociation energies of H---CH=CHOH, CH_2=C(OH)---H, CH_2=CHO---H, H---CH=$CHOCH_3$, CH_2=C(OCH_3)---H, CH_2=$CHOCH_2$---H is presented in Table 2.31. They are estimated using the $\Delta H^\circ_{f\ 298}$ values of vinyl alcohols, methyl vinyl ether, and corresponding radicals from this work.

The bond dissociation energies (kcal/mol) for vinyl alcohol and methyl vinyl ether are in scheme 2 below.

Scheme 2

Vinyl alcohol species	H---CH=CHOH	CH_2=COH---H	CH_2=CHO---H.
Bond dissociation energy	114.15	108.18	85.74
Methyl vinyl ether species	H---CH=$CHOCH_3$	CH_2=C---$HOCH_3$	CH_2=$CHOCH_2$---H
Bond dissociation energy	114.06	109.31	98.96

2.4.6 Hydrogen Bond Increment Group Value For Radicals

A method to estimate thermochemical properties for radicals from the corresponding properties of the parent with a H atom bonded to the radical site using a single group to modify the parent properties (hydrogen bond increment (HBI) group) has been reported by Lay et al [32]. HBI group values are derived for the vinyl alcohol and methyl vinyl ethers radicals in this study, using the thermodynamic properties data of radicals corresponding to loss of a H atom from the parent vinyl alcohol and methyl vinyl ether. Hydrogen Bond Increment (HBI) values are derived from calculated properties of radicals (C·H=CHOH, CH_2=C·OH, C·H=$CHOCH_3$, CH_2=C·OCH_3, and CH_2=CHOC·H_2) and the respective parent. A hydrogen atom bond increment (HBI) group for $DH_{f\ (298)}$ reflects the enthalpy change due to loss of a H atom from a stable parent molecule in the form of the R-H bond energy. As an example, the bond energy of H---CH=CHOH is based on the heat of formation of the following H-bond dissociation reaction:

$(CH_2{=}CHOH)$ = (C·H=CHOH) + H $\Delta H_{f,(298)}$ = D (H---CH=CHOH)

The DH $_{f\ 298}$ value of D (H---CH=CHOH) is 114.15 kcal/mol and data is listed in Table 2.13 for all radicals in this study.

ΔS_{298} and $\Delta C_p(T)$ are determined more directly, as the differences in respective properties of the molecule versus the radical in such a way that the HBI values for S_{298} and $C_p(T)$ are added to the parent values to form the radical.

Heat capacity is the most straightforward, as it is a simple difference in the corresponding $C_p(T)$ properties:

$C_p(T_i)$ (C·H=CHOH) = $C_p(T_i)(CH_2{=}CHOH)$ + HBI($C_p(T_i)$(C·H=CHOH))

The contributions corresponding to change in symmetry between the radical and parent are not included in the HBI group but are included in evaluation of the entropy of each species separately. The number of optical isomers does not change for these vinyl alcohols or methyl vinyl ether species.

The HBI group value of ΔS_{298} for C·H=CHOH can be written as

HBI S_{298} (C·H=CHOH) = [S_{298} (C·H=CHOH) +R ln $\sigma_{C\cdot H=CHOH}$] - [S_{298} (CH_2=CHOH) R ln $\sigma_{CH2=CHOH}$]

Here σ represents symmetry and it is applied separately to both the radical and the parent molecule. Degeneracy of the radical electronic state is included in HBI group.

The data of HBI groups for vinyl alcohols and methyl vinyl ethers is listed in Table 2.13. The $C_p(T)$ and S_{298} values in the Hydrogen Bond Increment Group correspond to contributions from loss of three vibration frequencies, loss of H atom plus changes in moments of inertia, and internal rotors.

Table 2.13 $\Delta H_f^\circ{}_{(298)}$, Entropy and Heat Capacities of HBI[a]

Species	$\Delta H_f^\circ{}_{(298)}$[b]	S[c]	C_p[c]: 300	400	500	600	800	1000	1500
CJ=COH[d]	114.15	1.31	0.01	-0.41	-0.97	-1.56	-2.6	-3.33	-4.45
C=CJOH[e]	108.18	2.77	-0.74	-1.86	-2.68	-3.23	-3.9	-4.27	-4.89
C=COJ[f]	85.74	0.10	-2.22	-3.03	-3.43	-3.59	-3.6	-3.66	-3.9
CJ=COC[g]	114.06	3.19	-0.54	-1.44	-2.8	-4.44	-7.8	-10.8	-15.91
C=CJOC[h]	109.31	3.64	-1.2	-2.52	-3.31	-3.76	-4.2	-4.52	-4.98
C=COCJ[i]	98.96	3.87	-0.78	-1.19	-1.52	-1.84	-2.5	-3.09	-4.17

[a] HBI group (parent and radical molecule) = hydrogen bond increment. [b] Units = kcal/mol. [c] Units in cal/(mol K). [d] CJ=COH = D(H---CH=CHOH) [e] C=CJOH = D(CH_2=C(OH)---H) [f] C=COJ D(CH_2=CHO---H) [g] CJ=COC = D(H---CH=$CHOCH_3$) [h] C=CJOC = D(CH_2=C(OCH_3)---H) [i] C=COCJ D(CH_2=$CHOCH_2$---H) *Notes : 1. CJ is C·*

2.4.7 Group Additivity Values (O/C_D/H and O/C_D/H)

Group additivity is straightforward and a reasonably accurate method for estimating the thermochemical properties of hydrocarbons and oxygenated hydrocarbons. It is particularly useful for large molecules where high-level ab intio or density functional calculations are not practical. The thermochemical properties of vinyl alcohol and methyl vinyl ether needed to calculate group additivity values are listed in Table 2.14.

C_D/H/O and O/C_D/H are two groups in every vinyl alcohol species. The $\Delta H^\circ{}_{f\ 298}$ value of the C_D/H/O group, 8.6 kcal/mol, is assigned by Benson [30]; it is also used by Holmes, [31] Turecek, [4] Li Zhu et al,[8] and Cohen.[32] The $\Delta H^\circ{}_{f\ 298}$ of the O/C_D/H group is calculated to be -44.6 kcal/mol by Holmes, [34] -48.28 by Turecek, [4] -46.30 by Li Zhu et al, [8] and -49.3 by Cohen. [32] These values ($\Delta H^\circ{}_{f\ (298)}$ of the O/C_D/H group) are significantly lower than Benson's [30] assignment of -37.9 kcal/mol based on O/C_D/H in alcohols. In this work, group values of the O/C_D/H (Table 2.15) are calculated by using the syn conformers of vinyl alcohol (CH_2=CHOH) and methyl vinyl ether (CH_2=$CHOCH_3$).

Group additivity uses the sum of the groups to represent the value of the target molecule(s):

$$\Delta H^{\circ}_{f\,298}\,(CH_2{=}CHOH) = \Delta H^{\circ}_{f\,298}(C_D/H_2) + \Delta H^{\circ}_{f\,298}\,(C_D/H/O) + \Delta H^{\circ}_{f\,298}\,\mathbf{(O/C_D/H)}$$

$$\Delta H^{\circ}_{f\,298}\,(CH_2{=}CHOCH_3) = \Delta H^{\circ}_{f\,298}(C_D/H_2) + \Delta H^{\circ}_{f\,298}\,(C_D/H/O) + \Delta H^{\circ}_{f\,298}\,(C/H_3/O) + \Delta H^{\circ}_{f\,298}\,\mathbf{(O/C/C_D)}$$

Bold = target groups

The values for the known groups C_D/H_2, $C/H_3/O$ in these reactions are summarized in Table 2.15. The enthalpy values of the $O/C_D/H$ and $O/C/C_D$ groups are calculated to be -44.57 kcal/mol and –29.80 kcal/mol respectively. This $O/C_D/H$ value is close to the data of Holmes.[31] but 3.7 kcal/mole higher than values of Turecek [4] and Cohen. [32] and 1.4 kcal/mole higher than values of Zhu and Bozzelli.[8] The enthalpy values (298) of the $O/C/C_D$ groups is 0.7 kcal/mole higher than values of Cohen [32] and Benson.[30] The entropy and the heat capacity terms of the $O/C_D/H$ group are calculated from $CH_2{=}CHOH$.

Groups	$\Delta H^{\circ}_{892\ \phi}$	S°_{298}	**C_p: 300**	**400**	**500**	**600**	**800**	**1000**	**5000**	**Reference**
$O/C/C_D$	-29.80	5.44	4.04	4.73	4.99	5.04	4.97	4.81	4.49	In this work
$O/C/C_D$ [a]	-29.69	6.75	3.84	4.57	4.86	4.95	4.89	4.73	4.42	Anti In this work
$O/C/C_D$										Benson (ref 29)
$O/C/C_D$	-30.50									Cohen (ref 31)
Groups	$\Delta H^{\circ}_{892\ \phi}$	S°_{298}	**C_p: 300**	**400**	**500**	**600**	**800**	**1000**	**5000**	**Reference**
$O/C_D/H$	-44.57	26.12	5.52	6.79	7.44	7.74	7.94	8.02	8.36	In this work
$O/C_D/H$ [a]	-44.42	27.30	5.46	6.72	7.36	7.67	7.87	7.96	8.29	Anti In this work
$O/C_D/H$	-44.60									Holmes (ref 30)
$O/C_D/H$	-48.28									Turecek (ref 3)
$O/C_D/H$	-49.30									Cohen (ref 31)
$O/C_D/H$	-37.90									Benson (ref 29)

a = anti group

$X(O/C_D/H) = X(CH_2{=}CHOH) - X(C_D/H_2) - X(C_D/H/O)$[7]

where $X = S°_{298}$ and C_p.

The $O/C_D/H$ and $O/C/C_D$ group (for group additivity) are evaluated from syn vinyl alcohol ($CH_2{=}CHOH$) and syn vinyl ether ($CH_2{=}CHOCH_3$) and compared with literature data.

They are also evaluated by using anti group value of syn and anti conformations of vinyl alcohol ($CH_2{=}CHOH$) and methyl vinyl ether ($CH_2{=}CHOCH_3$). The $\Delta H°_{f\ 298}$ value of anti $O/C_D/H$ is –44.42 kcal/mol, which is 0.15 kcal/mol higher than the value (-44.57 kcal/mol) of anti $O/C_D/H$ calculated by using syn vinyl alcohol ($CH_2{=}CHOH$) and methyl vinyl ether ($CH_2{=}CHOCH_3$). The $\Delta H°_{f\ 298}$ value of anti $O/C/C_D$ group is -29.69 kcal/mol, which is 0.11 which is 0.15 kcal/mol higher than the value (-44.57 kcal/mol) of anti $O/C/C_D$ calculated by using syn vinyl alcohol ($CH_2{=}CHOH$) and methyl vinyl ether ($CH_2{=}CHOCH_3$).

Table 2.14 $\Delta H_f°_{(298)}$, Entropy and Heat Capacities of Each Molecule[a]

Species		$\Delta H_f°_{(298)}$ [b]	S[c]	C_p[c]: 300	400	500	600	800	1000	1500
Anti $CH_2{=}CHOH$	TVR[d]		60.28	12.1	15	17.6	19.7	23.04	25.51	29.52
	I.R1[e]		1.45	2.68	3.12	3.16	3.01	2.57	2.19	1.62
	Total[f]	-27.96±0.14	61.73	14.8	18.2	20.8	22.7	25.61	27.69	31.15
Syn $CH_2{=}CHOH$	TVR[d]		61.68	12.1	15	17.6	19.7	23.03	25.51	29.53
	I.R1[e]		1.45	2.68	3.12	3.16	3.01	2.57	2.19	1.62
	Total[f]	-29.71±0.15	63.13	14.8	18.1	20.7	22.7	25.6	27.7	31.15
Anti $CH_2{=}CHOCH_3$	TVR[d]		62.41	14.6	18.8	22.9	26.3	31.87	36	42.47
	I.R1[e]		5.42	1.5	1.32	1.22	1.16	1.09	1.06	1.02
	I.R2[e]		3.63	3.48	3.77	3.63	3.34	2.71	2.19	1.36
	Total[f]	-23.48±0.45	71.46	19.5	23.9	27.7	30.8	35.67	39.25	44.86
Syn $CH_2{=}CHOCH_3$	TVR[d]		63.85	14.4	18.7	22.7	26.3	31.8	35.94	42.43
	I.R1[e]		5.42	1.5	1.32	1.22	1.16	1.09	1.06	1.02
	I.R2[e]		3.63	3.48	3.77	3.63	3.34	2.71	2.19	1.36
	Total[f]	-25.02±0.42	72.9	19.3	23.8	27.6	30.8	35.6	39.19	44.81

[a] Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm, optimized at the B3lyp/6-31G(d,p) level of theory. Then it is calculated by computer code (SMCPS45). [b] Units in kcal/mol. [c] Units in cal/(mol k).. [d] The sum of contributions from translations, external rotations, and vibrations. [e] Contribution from internal rotation about the C-O and O-C. [f] Total = TVR + I.R1 + I.R2.

Table 2.15 Group Values

Groups	$\Delta H_f°_{(298)}$[a]	$S°_{298}$[b]	C_p[b]: 300	400	500	600	800	1000	1500
C_D/H_2[c]	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
$C/H_3/O$[d]	-10.08	30.41	6.19	7.84	9.40	10.79	13.03	14.77	17.58
$C_D/H/O$[f]	8.60	8.00	4.20	5.00	5.80	6.50	7.60	8.40	9.60
Group calculated									
$O/C_D/H$	-44.57	26.12	5.52	6.79	7.44	7.74	7.94	8.02	8.36
Anti Group $O/C_D/H$[g]	-44.42	27.30	5.46	6.72	7.36	7.67	7.87	7.96	8.29
$O/C/C_D$	-29.80	5.44	4.04	4.73	4.99	5.04	4.97	4.81	4.49
Anti Group $O/C/C_D$[g]	-29.69	6.75	3.84	4.57	4.86	4.95	4.89	4.73	4.42

[a] $\Delta H°_{f\,298}$ in kcal/mol, [b] $S°_{298}$ and C_p in cal/mol k. [c] Chen and Bozzelli[33]. [d] Benson[29]. [f] Li Zhu et al [7] [g] Anti Group = values added to syn group to obtain values of anti conformer.

CHAPTER 3

KINETIC ANALYSIS OF NEOPENTYL RADICAL REACTION WITH MOLECULAR OXYGEN

3.1 Overview

Neopentyl radical reaction with oxygen, which has a several reaction channel and makes a variety product, is estimated by computational chemistry method. Thermodynamic properties on reactants, intermediates, products and important transition states are calculated and a thermochemical kinetic analysis performed for reaction of neopentyl radical with O_2. The reaction forms a chemically activated $C_3CCOO\bullet$ adduct, which can be stabilized, dissociate back to reactants or isomerize to a hydroperoxide alkyl radical and make $C_3CC{=}O$ + OH product. The isomer can dissociate to CH_3 + $C{=}C(C)COOH$, to a cyclic ether ($C_2CyCCOC$) + OH, and to OH + CH_2O + $C{=}C(C_2)$, isomerize back to the peroxy, or further react with O_2. Kinetics are analyzed with Quantum RRK theory for k(E) coupled with modified strong collision analysis of Gilbert et al for fall-off.

Two features of neopentyl facilitate a simpler interpretation of results, relatived to most alkyl radical oxygen reaction systems. i. All the C-H bonds are identical so that only one species of alkyl radicals involved ii. The carbon atom radical site is connected to a carbon with no hydrogen atoms, thus, unlike the majority of alkyl radicals, the formation of the conjugate alkenes by a more direct abstraction of H by O_2, not involving radical isomerization, is structurally impossible reaction of stabilization, reverse dissociation, isomerization and isomer decomposition are dominant here.

3.2 Background

There are two experimental studies, which focus on neopentyl radical oxidation. [51, 52] One study on the equilibrium and thermodynamic aspects of the reaction [53] and two studies [54, 55] at low pressure on kinetics of the initial neopentyl peroxy radical formation.

Hughes et al studied formation of OH radical from thermal decomposition of neopentyl iodide in a bath of He with varied concentrations of O_2 at pressures of 575 to 660 Torr and at temperature from 660 to 750 K. OH radical product concentration profile versus time was monitored and fit to bi-exponential growth curves. An exact analytical solution was postulated incorporating peroxy formation, reverse dissociation, isomerization (hydrogen atom transfer, but non-reversible), and only one isomer decomposition product channel – cyclic ether + OH. Hughes et al concluded that he above reaction processes were the only important components to include in their analysis, that the isomerization process had the controlling barrier for the overall reaction process. They also indicated the kinetics and pathways for adduct formation, reverse decomposition, isomerixation and subsequent hydroperoxide alkylradical decompositions were in good agreement with previous studies of the Baldwin and Walker research group. [52] Hughes et al reported rate constants for the isomerization with A of 1.58×10^{12} and E_a of 29 kcal/mole. This results in a high Ea of 17 kcal/mol for the reverse reaction, which is 12.5 kcal/mol exothermic and has 6 member ring transition state usually considered to have about 1 – 2 kcal/mol of strain.

The research group of Baldwin and Walker [52] studied reactions of neopentyl radical derived from neopentane in an atmosphere of hydrogen and oxygen at temperature from 653 to 793 K, in a flow reactor (aged,boric-acid-coated Pyrex) with reaction times ranging up to several tens of seconds. They report stable products as a function of oxygen concentration at temperature from 653 to 793 K and analyzed the data using steady state and equilibrium relationships. They concluded that the reactions of neopentyl radicals in an oxidizing environment involve a relatively small mechanism, which provided quantitative interpretation of product yields. The initial products detected, at their conditions, were 3,3-dimethyloxetane(DMO), acetone, isobutene, and formaldhyde. They determined Arrhenius parameters for elementary reactions in their mechanism via extrapolation of product ratios (acetone + DMO / I-butene) and aceton/ DMO, which were measured using a gas chromatography at each temperature. Arrhenius expressions for their 1,5p H-atom transfer (where p represents primary) in neopentylperoxy radical and 1,4p H-atom transfer in ethylperoxy radical [56], were combined with thermochemical calculation to estimate Arrhenius parameters for primary, secondary and tertiary intramolecular H-atom transfers in alkyperoxy radicals involving 4 to 8 member cyclic transtion states (at 753k).

Slagle et al [54] studies the loss of neopentyl radical using a heated tubular tractor coupled to a photoionization mass spectrometer over a 1 to 10 Torr oressure range. They producted neopentyl radical indirectly by pulsed exicimer laser photolysis of CCl_4 (to product CCl_3+Cl) followed by the rapid reaction between the Cl atoms and neopentane to produce neo-C_5H_{11} + HCl. Neo-C_5H_{12} concentrations were high enough to "convert" the Cl atoms to neo-C5H11radicals within 0.5 ms and neo-C_5H_{11} concentrations were low (typically in the range (1-6) * 10^{10} molecules cm^{-3}). This was achieved by selecting the initial conditions (CCl_4 concentration and laser intensity) so that reactions between photolysis products (including the C_5H_{11} + C_5H_{11} recombination reaction) had negligible rates compared to that of the unimolecular decomposition process under study. They monitored decomposition of neo-C_5H_{11} radical at various temperatures (560 to 650 k) allowing an enthalpy of reaction to be derived. They also modeled (RRKM) unimolecular decomposition of neo-C_5H_{11} to isobutene + methyl radical and determined a 31 kcal/mol barrier and an A factor of 7.94 $x10^{13}$, both the E_a and A factor compare well with data obtained by Baldwin [51] and Furimsky.[57]

The research group of Bayes et al [54, 55] studied the rate constants on reaction of neopentyl radical with O2 at 266 to 374 K and low pressure, 3 to 3.5 Torr. They monitored the pseudo-first-order decay of the neopentyl radicals as a function of oxygen, using a mass spectrometric detection. Neopentyl radicals were produced by the laser flash photolysis of neopentyl bromide using an ArF laser at 193 nm, or by the two steps method described above in Slagle's experiment (first, chlorine atom, then neopentyl radicals). [53] Their experimental results show a negative temperature dependence for the rate constant of neopentyl radical with O_2. They used adiabatic channel model calculation to interpret their results and reported the rate constant of this reaction as $K= (1.265 \text{ x } 10^{12} \text{ cm}^3 \text{ /mol s})(T/300K)^{-(2.1\pm0.4)}$, with no fall-off analysis.

Curran et al [58] have recently published a kinetic model to analyze experimental results, obtained by Baker et al, [59, 60] on the oxidation of neopentane in a closed reactor at 500 Torr and one temperature 753 k. the rate constants model stable species profile well and are presented as part of a very large, - several thousand reaction -, hydrocarbon oxidation model. They estimate kinetic parameters for some paths this study analyze; then focus on subsequent reactions of initial product radicals and show good agreement for stable end-product profiles. They do not include transition state analysis, or rate constant fall-off.

Treatment of the energized complex reactions included analysis of decomposition back to reactants, intramolecular transfer of hydrogen atoms to form hydroperoxy radicals which further decompose to $C_2CyCCOC$ + OH, C=C(C)COOH + C_3H, C_2C=C + C• H_2OOH, C_3CC=CO +OH, before stabilization to ground state peroxy or hydroperoxy radicals. Further reactions of the stabilized peroxy radicals include: dissociation to reactants, or isomerization to hydroperoxy via H shift and then beta scission to final products, or addition of a second O_2. Several other important reaction paths are also accounted in the elementary reaction mechanism. This research focuses on; the reversible peroxy formation, the isomerization channels and the OH formation path.

Enthalpies of reactants, intermediates, products and transition states for the elementary reactions resulting from addition of neopentyl radical to molecular oxygen are evaluated and are illustrated in Figure 4. High-pressure rate constants are evaluated from literature or from calculated TST structures. Quantum RRK theory [61 - 63] is used to calculate K(E) with the modified strong collision of Gilbert et al [64] used to calculate fall off effects in a kinetic analysis on the chemical activation reaction systems. The rate constants are incorporated into a detailed, elementary reaction mechanism, which is used to model experimental results of Hughes et al.

This study model contains 58 reactions and 39 species and is shown to describe the above experimental data well; but it is significantly different in description of the neopentyl + O_2 reaction from that of Hughes et al, and of Baldwin and Walker. [52] It shows that an isomerization barrier height some 7 kcal /mol lower that that of the above two research groups and that subsequent barriers are responsible for the apparent barrier reported by Hughes et al. This study also shows that while one reaction is responsible for a major fraction of the OH formation – (more than half), the total OH is actual the result of several reaction paths. Importance of these paths will change with varied concentrations, pressure and temperature. This study also shows that reactions of hydroperoxy-neopentyl radical with oxygen can have significant contributions to the OH profile.

At temperature, above 1200 C unimolecular dissociation of the neopentyl radical is the primary reaction, relative to reaction with O_2. The discussion in this work focuses on temperatures where reaction with oxygen is important.

3.3 Thermodynamic Properties

The addition reactions and subsequent unimolecular isomerization or dissociation reactions are analyzed by construction of potential energy diagram of the systems based on existing theoretical data.

3.3.1 Calculation Methods

The structural parameters are fully optimized at the B3LYP/6-31g(d,p) level theory. The harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. The optimized geometrical parameters are used to obtain total electronic energies at B3LYP/6-31g(d,p), B3LYP/6-311+G(3df,2p), and CBS-Q//B3LYP/6-31G(d,p) calculations levels.

3.3.2 Geometries and Vibrational Frequencies

The fully optimized geometries at the B3LYP/6-31g(d,p) density functional calculation level for $C_3CCOO\cdot$, $C_3\cdot CCOOH$, and the transition states are listed in Figures 1 through 7 and Tables 1 through 7.

Harmonic vibrational frequencies and moments of inertia are calculated for each molecule at the B3LYP/6-31g(d,p) level on the basis of optimized geometries at this same level of theory. It is listed in Table 8 and Table 9.

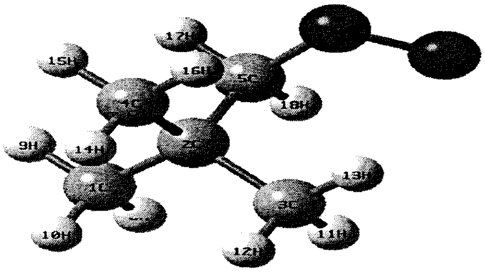


Figure 3.1 B3lyp/6-31G(d,p) optimized geometries of $C_3CCOO\bullet$

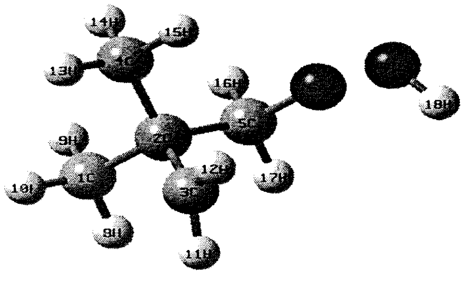


Figure 3.2 B3lyp/6-31G(d,p) optimized geometries of $C_3\bullet CCOOH$

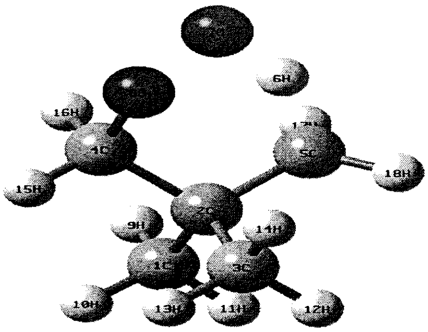


Figure 3.3 B3lyp/6-31G(d,p) optimized geometries of Ts1

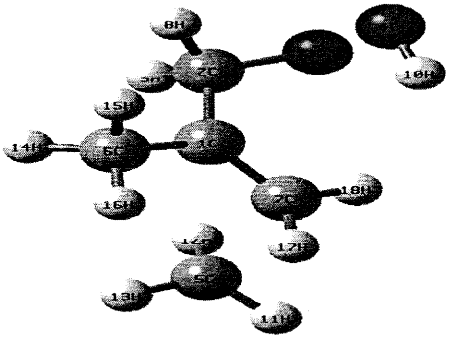


Figure 3.4 B3lyp/6-31G(d,p) optimized geometries of Ts2

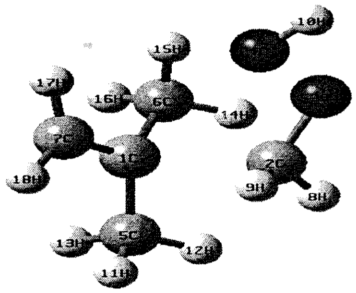


Figure 3.5 B3lyp/6-31G(d,p) optimized geometries of Ts3

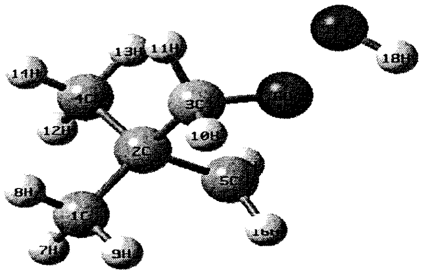


Figure 3.6 B3lyp/6-31G(d,p) optimized geometries of Ts4

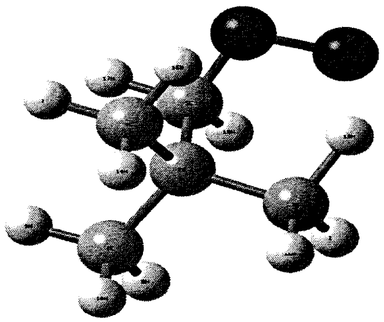


Figure 3.7 B3lyp/6-31G(d,p) optimized geometries of Ts5

3.3.3 Enthalpies of Formation ($\Delta H^\circ_{f\,298}$)

Enthalpies of formation ($\Delta H^\circ_{f\ 298}$) are estimated using total energies and calculated enthalpies of reaction (ΔH°_{rxn}) for the listed reactions. ΔH°_{rxn} for each reaction is calculate using evaluated literature thermodynamic properties for these reference reactants and product by using the working reaction. The total energies at 298 K at B3LYP/6-31G(d,p) and ZPVE, thermal correction to 298.15 K are listed in Table 10.

As example, one reaction used to calculated $\Delta H^\circ_{f\,298}$ (Neopentyl-OO•) is:

$$\text{Neopentyl-OO}\cdot + CH_3CH_2CH_2OOH \rightarrow CH_3CH_2CH_2OO\cdot + \text{Neopentyl-OOH}$$

$$\begin{aligned}\Delta H^\circ_{f\,298} = {} & \Delta H^\circ_{f\,298}(\text{Neopentyl-OOH}) + \Delta H^\circ_{f\,298}(CH_3CH_2CH_2OO\cdot) \\ & - (\Delta H^\circ_{f\,298}(\text{Neopentyl-OO}\cdot) + \Delta H^\circ_{f\,298}(CH_3CH_2CH_2OOH))\end{aligned}$$

The reaction enthalpies and $\Delta H^\circ_{f\ 298}$ of this molecule (Neopentyl-OO•) obtained from using of the reaction are tabulated in Table 11.

Table 3.1 Total Energy, ZPVE, and Thermal Corrections and Energy Values

Species	ZPVE[a]	Thermal. correction[b].	Total Energy		
			B3LYP/6-31[c]	B3LYP/6-311[d]	CBS-Q[e]
$C_3CCOO\cdot$	0.15646	0.00963	-347.33	-347.48	-347.16
$C_3\cdot CCOOH$	0.15296	0.01062	-347.29	-347.41	-347.08
Ts1	0.15029	0.00876	-347.29	-347.4	-347.07
Ts2	0.15073	0.01009	-347.21	-347.33	-347.07
Ts3	0.14996	0.01092	-347.26	-347.37	-347.1
Ts4	0.15201	0.00996	-347.27	-347.39	-347.11
Ts5	0.15167	0.001	-347.21	-347.33	-347.12

[a] ZPVE : scaled zero-point energies in Hartree (scaled by 0.9806) [b] Therm. corr. : Thermal corrections in Hartree. [c] B3lyp/6-31G(d,p). Total energies are in Hartree at 0 K. [d] B3lyp/6-311+G(3df,2p). [e] CBS-Q enthalpies are in Hartree, which include thermal correction and zero point energy at 298.15 K.

Table 3.2 Enthalpies of Formation for Neopentyl Adduct and Transition State

Isodesmic Reaction	Heat of Reaction			Heat of Formation		
	B3LYP /6–31G(d,p)	B3LYP/6-311++G(2fd,2p)	CBS-Q	B3LYP /6–31G(d,p)	B3LYP/6-311++G(2fd,2p)	CBS-Q
$C_3CCOO\cdot$+ cccooh = cccooj + c3ccooh	0.334	0.331	0.327	-26.43	-25.39	-25.4
$C_3\cdot CCOOH$ +cccooh = cjccooh+c3ccooh	-0.738	-0.72	-0.71	-12.67	-12.49	-12.52
$C(C_3H_9)CCOO\cdot$ = **TS1**	23.99	24.29	24.31	-1.57	-1.87	-1.89
$C\cdot H_2(C_2H_6)CCOOH$ = **TS2**	31.02	29.86	28.83	21.57	20.41	19.38
$C\cdot H_2(C_2H_6)CCOOH$ = **TS3**	24.03	22.68	22.28	15.67	14.32	13.92
$C\cdot H_2(C_2H_6)CCOOH$ = **TS4**	14.57	14.07	13.34	5.94	5.04	4.71
$C(C_3H_9)CCOO\cdot$ = **TS5**	29.67			18.47		

3.3.4 Rotational Barriers

The potential barriers for internal rotations of each molecule ((C_3CCOO·, C_3·CCOOH, Ts1, Ts2, Ts3, Ts4, and Ts5) are calculated at the B3LYP/6-31g(d,p) density functional calculation level. The potential energy as function of dihedral angle is determined by scanning the torsion angles from 0 to 360 at 15 intervals and allowing the remaining molecular structural parameters to be optimized. The geometry and harmonic vibrational frequencies are calculated for all rotational conformers at B3LYP/6-31g(d,p) level. The barriers for internal rotations are calculated from the differences between the total energy of each conformer as a function of torsional angle in 15degree intervals. It is listed in Tables 3 through 6 and Figures 1 through 17.

Table 3.3 Total Energy and Internal Rotation Barriers C_3CCOO·

	C-C(C_2)COOJ	C(C_3)-COOJ	(C_3)CC-OOJ
Torsion Angle	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)
0	0	0	0
15	0.44	0.63	0.01
30	1.6	2.27	0.68
45	2.84	4.14	0.17
60	3.41	4.88	0.25
75	2.87	3.9	0.38
90	1.64	2.05	0.39
105	0.48	0.56	0.23
120	0	0	0
135	0.44	0.63	0.01
150	1.6	2.27	0.68
165	2.84	4.14	0.17
180	3.41	4.88	0.25
195	2.87	3.9	0.38
210	1.64	2.05	0.39
225	1.6	0.56	0.23
240	2.84	0	0
255	3.41	0.63	0.01
270	2.87	2.27	0.68
285	1.64	4.14	0.17
300	3.41	4.88	0.25
315	2.87	3.9	0.38
330	1.64	2.05	0.39
345	0.48	0.56	0.23
360	0	0	0

Table 3.4 Total Energy and Internal Rotation Barriers C_3·CCOOH

	cjc(c2)co-oh	cjc(c2)c-ooh	cjc(c2)-cooh	cj-c(c2)cooh	cjc-(c2)cooh
Torsion Angle	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)
0	0	0	0	0	0
15	0.03	0.31	0.63	0.23	0.45
30	0.39	1	2.27	0.28	1.59
45	1.18	1.61	4.14	0.31	2.83
60	2.4	1.63	4.88	0.29	3.38
75	3.83	0.82	3.9	0.31	2.81
90	5.02	0.24	2.05	0.28	1.57
105	5.48	0.57	0.56	0.14	0.46
120	5.02	0	0	0	0
135	3.83	0.31	0.63	0.23	0.45
150	2.4	1	2.27	0.28	2.81
165	1.18	1.61	4.14	0.31	1.57
180	0.39	1.63	4.88	0.29	0.46
195	0.03	0.82	3.9	0.31	0
210	0.05	0.24	2.05	0.28	0.45
225	0.36	0.57	0.56	0.14	0.46
240	0.82	0	0	0	0
255	1.28	0.31	0.63	0.23	0.45
270	1.63	1	2.27	0.28	1.59
285	1.76	1.61	4.14	0.31	2.83
300	1.63	1.63	4.88	0.29	3.38
315	1.28	0.82	3.9	0.31	2.81
330	0.82	0.24	2.05	0.28	1.57
345	0.36	0.57	0.56	0.14	0.46
360	0	0	0	0	0

Table 3.5 Total Energy and Internal Rotation Barriers Ts1 and Ts2 (C~~C(C_2)COOH)

	Ts1	c~~c-(c2)cooh	c~~c(c2)-cooh	c~~c(c2)c-ooh	c~~c(c2)co-oh
Torsion Angle	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)
0	0.00	0.00	0.00	0.00	0.00
15	1.09	0.03	0.63	0.31	0.03
30	2.34	0.09	2.27	1.00	0.39
45	2.95	0.07	4.14	1.61	1.18
60	2.45	0.02	4.88	1.63	2.40
75	1.24	0.08	3.90	0.82	3.83
90	0.09	0.08	2.05	0.24	5.02
105	4.83	0.05	0.56	0.57	5.48
120	0.00	0.00	0.00	0.00	5.02
135	1.09	0.03	0.63	0.31	3.83
150	2.34	0.09	2.27	1.00	2.40
165	2.95	0.07	4.14	1.61	1.18
180	2.45	0.02	4.88	1.63	0.39
195	1.24	0.08	3.90	0.82	0.03
210	0.09	0.08	2.05	0.24	0.05
225	4.83	0.05	0.56	0.57	0.36
240	0.00	0.00	0.00	0.00	0.82
255	1.09	0.03	0.63	0.31	1.28
270	2.34	0.09	2.27	1.00	1.63
285	2.95	0.07	4.14	1.61	1.76
300	2.45	0.02	4.88	1.63	1.63
315	1.24	0.08	3.90	0.82	1.28
330	0.09	0.08	2.05	0.24	0.82
345	4.83	0.05	0.56	0.57	0.36
360	0.00	0.00	0.00	0.00	0.05

Table 3.6 Total Energy and Internal Rotation Barriers Ts3, Ts4, and Ts5

	Ts3	Ts3	ts4	Ts5	Ts5
	cj-c(c2)~~cooh	cjc-(c2)~~cooh			
Torsion Angle	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)	E(kcal/mole)
0	0	0	0	0	0
15	0.23	0.45	0.01	0.44	0.63
30	0.28	1.59	0.83	1.6	2.27
45	0.31	2.83	2.08	2.84	4.14
60	0.29	3.38	3.04	3.41	4.88
75	0.31	2.81	3.03	2.87	3.9
90	0.28	1.57	2.09	1.64	2.05
105	0.14	0.46	0.85	0.48	0.56
120	0	0	0.02	0	0
135	0.23	0.45	0.01	0.44	0.63
150	0.28	2.81	0.84	1.6	2.27
165	0.31	1.57	2.1	2.84	4.14
180	0.29	0.46	3.04	3.41	4.88
195	0.31	0	3.03	2.87	3.9
210	0.28	0.45	2.08	1.64	2.05
225	0.14	0.46	0.84	1.6	0.56
240	0	0	0.03	2.84	0
255	0.23	0.45	0.01	3.41	0.63
270	0.28	1.59	0.77	2.87	2.27
285	0.31	2.83	2.03	1.64	4.14
300	0.29	3.38	3.03	3.41	4.88
315	0.31	2.81	3.02	2.87	3.9
330	0.28	1.57	2.03	1.64	2.05
345	0.14	0.46	0.78	0.48	0.56
360	0	0	0	0	0

3.3.5 Entropy, $S°_{298}$ and Heat Capacity, $C_p(T)$ from 300 to 1500 K

$S°_{298}$ and $C_p(T)$'s calculation results using B3LYP/6-31g(d,p) determined geometries and frequencies are summarized in Table 7. Moment of inertia of all of them is presented in Table 9. TVR represents the sum of the contributions from translations, rotations and vibrations for $S°_{298}$ and $C_p(T)$'s. The torsion frequencies calculated for the internal rotors are not included in TVR. Instead, a more exact contribution from hindered rotations is calculated. I.R., represents the contributions from the internal rotation about carbon-oxygen and carbon-carbon bonds for $S°_{298}$ and $C_p(T)$'s. The final standard entropies also include correction terms for rotational conformers. This correction is calculated by the following formula for 1 mole of mixture[49]:

$$\Delta S_{mixing} = -R\Sigma n_i \ln(n_i)$$

where n_i is the equilibrium mole fraction of the ith form. ΔS_{mixing} represents the entropy of mixing of rotational conformations or optical conformations.

Table 3.7 $\Delta H_f°_{(298)}$, Entropy, and Heat Capacities of each molecule

Species		ΔH_{298}	S	Cp: 300	400	500	600	800	1000	1500
$C_3CCOO\cdot$	TVR			24.38	32.57	40.18	46.77	57.16	64.85	76.77
	I.R1^e			2.75	2.69	2.43	2.16	1.76	1.51	1.24
	I.R2			2.75	2.69	2.43	2.16	1.76	1.51	1.24
	I.R3			2.75	2.69	2.43	2.16	1.76	1.51	1.24
	I.R4			2.08	2.07	1.99	1.85	1.50	1.18	0.66
	I.R5			1.11	1.04	0.98	0.91	0.75	0.61	0.37
	Total	-25.4	69.28	35.81	11.19	10.27	9.25	7.53	6.33	4.74
$C_3\cdot CCOOH$	TVR			25.43	33.43	40.67	46.83	56.49	63.67	75.00
	I.R1			1.02	1.01	1.01	1.00	1.00	1.00	1.00
	I.R2			2.76	2.39	2.11	1.89	1.59	1.42	1.21
	I.R3			2.76	2.39	2.11	1.89	1.59	1.42	1.21
	I.R4			2.09	2.09	2.01	1.87	1.52	1.20	0.67
	I.R5			1.88	1.54	1.27	1.06	0.75	0.55	0.29
	I.R6			1.99	1.92	1.82	1.73	1.58	1.47	1.28
	Total	-12.52	75.83	12.49	11.34	10.32	9.44	8.04	7.05	5.66
Ts1	TVR			26.85	35.88	43.90	50.63	60.96	68.42	79.77
	I.R1			1.30	1.17	1.11	1.08	1.04	1.01	0.92
	I.R2			1.30	1.17	1.11	1.08	1.04	1.01	0.92
	Total	-1.89	74.33	2.61	2.35	2.22	2.15	2.08	2.02	1.84
Ts2	TVR			23.66	31.85	39.15	45.32	54.96	62.11	73.33
	I.R1			0.99	0.99	0.99	0.99	0.99	0.99	0.99
	I.R2			0.99	0.99	0.99	0.99	0.99	0.99	0.99
	I.R3			2.09	2.09	2.01	1.87	1.52	1.20	0.67
	I.R4			1.88	1.54	1.27	1.06	0.75	0.55	0.29
	I.R5			1.99	1.92	1.82	1.73	1.58	1.47	1.28
	Total	19.38	73.47	7.95	7.53	7.09	6.64	5.84	5.20	4.24
Ts3	TVR			25.29	33.12	40.08	45.98	55.22	62.15	73.19
	I.R1			1.02	1.01	1.01	1.00	1.00	1.00	1.00
	I.R2			2.76	2.39	2.11	1.89	1.59	1.42	1.21
	I.R3			2.76	2.39	2.11	1.89	1.59	1.42	1.21
	Total	13.92	73.78	6.54	5.80	5.22	4.78	4.19	3.83	3.41
Ts4	TVR			29.12	37.52	44.90	51.09	60.71	67.82	79.06
	I.R1			2.14	2.19	2.09	1.95	1.69	1.50	1.25
	I.R2			2.14	2.19	2.09	1.95	1.69	1.50	1.25
	Total	4.71	77.78	4.28	4.37	4.19	3.91	3.38	3.01	2.51
Ts5	TVR			20.01	29.70	38.10	45.24	58.53	64.49	76.24
	I.R1^e			2.75	2.69	2.43	2.16	1.76	1.51	1.24
	I.R2			2.75	2.69	2.43	2.16	1.76	1.51	1.24
	I.R3			2.75	2.69	2.43	2.16	1.76	1.51	1.24
	I.R4			2.08	2.07	1.99	1.85	1.50	1.18	0.66
	Total	18.47	78.31	30.33	39.84	47.39	53.58	65.31	70.21	80.61

3.4 Kinetic Calculations

Branching ratio of the adduct formed from conbination, addition or insertion reactions to various product channels are calculated using a quantum version of RRK theory (QRRK) to evaluate energy dependent rate constants, k(E), of the adduct to the various channels. QRRK analysis, as initially presented by Dean [61, 70, 71] combined with the modified strong collision approach of Gilbert et al [64] are used to compute rate constants for both chemical activation and unimolecular reactions over a range of temperature and pressure.

A number of modifications have been made since the initially descriptions of the quantum RRK and fall-off calculations were published. [61, 62, 70, 71] These modifications [70] include:

- Use of a manifold of three vibration frequencies and respective degeneracies, plus incorporation of energies from one external rotation mode for the calculation of the ratio of the density states to the partition coefficient ρ(E)/Q(T) and for calculation of K(E) and of F(E).
- The F_E factor is now explicitly calculated for use in determining the collision efficiency β_c [64] in place of the previously assigned 1.15 value. The β_c is calculated from Gilbert et al eqn 4.7
- The Lennard-Jones collision frequency Z is calculated by: Z= Z integral , is obtained from fit of Reid et al. [74]

The QRRK analysis with the modified strong collision approach and constant F_E for fall-off has been used to analyze a variety of chemical activation reaction systems. [46, 75-82] It is shown to yield reasonable results in these applications, and provides a mechanism by which the effects of temperature and pressure can be evaluated and included in the kinetics.

An example of the fall off calculation compared to experimental and model (RRKM) data of the Gutman group [53] is illustrated in Figure 1 for unimolecular dissociation of the neopentyl radical at 0.0186 atm. This dissociation of neopetyl radical to isobutene plus methyl radical is important in this neopentyl + O_2 reaction analysis.

3.5 Input Data Requirements for The QRRK Calculations

Pre-exponential factors (Arrhenius A factors) in the high pressure limits, are obtained from experimental data in the literature and from this calculations. Transition state theory is utilized for isomerization, beta scission and addition reactions. [40] Activation energies are from endothermicity of reaction ΔU_{rxn} and from analogy to reactions with similar energetics, primarily ethyl and n-propyl radical reactions with O_2. The specific kinetic parameters are referenced in the tables associated with each reaction system.

Estimations are consistent and uniform throughout with reference to literature, experiment and / or calculation in all cases.

A reduced set of three frequencies and their associated degeneracies are computed from fits to heat capacity data, as described by Ritter. [41] These have been shown by Ritter to accurately reproduce molecular heat capacities, Cp, and by bozzelli et al [42] to yield accurate density of states $\rho(E)$ to partition coefficient (Q) ratios.

Lennard-Jones transport parameters, σ (Angstroms) and ε/κ (Kelvins), are obtained from tabulations [30] and from a calculation method based on molar volumes and compressibility. [43] The calculation formula is: $\sigma = (2.3551-0.087w)/(P_c/T_c)^{1/3}$ and

$\varepsilon/\kappa = (0.7915 + 0.1693w)T_c$, where w is molecular weight in gram/mol, P_c and T_c are the critical temperature and the critical pressure respectively.

Arrhenius A factors for the radical bimolecular combination at the high pressure limit are obtained from literature, and from trends in homologous series of these type reactions.

3.6 High Pressure Limit Rate Constants

Hydrogen transfer: $C_3CCOO\bullet \rightarrow C_3\bullet CCOOH$:

This reaction represents intramolecular, endothermic (12.88kcal/mol), transfer a H atom from a primary methyl carbon atom to the peroxy O radical site. The activation energy (E_a) for the forward reaction is estimated using the calculated results,

$A(T)=(ek/h)\times\exp(\Delta S^{\neq}(T)/R)$ in AT^n from

Where $\Delta S^{\neq}$ is calculated from $S^{\neq}{}_{\text{(transition state)}} - S_{\text{(reactants)}}$, $\Delta S^{\neq}{}_{\text{(transition state)}}$ is obtained from The calculations modified with entropy S(T) contributions from the internal rotors, electron spin (radicals) and correction for optical isomers.

Dissociation: $C_3CCOO\bullet \rightarrow C_3CC{=}O + OH$

The high pressure limit rate constant: A factor: 1.2279×10^{14}, n= 0.19304, $E_a = 43.06$

Dissociation: $C_3\bullet CCOOH \rightarrow CH_3 + C{=}C(C)COOH$

The high pressure limit rate constant: A factor: 4.8733×10^{14}, n= -1.02461, $E_a = 29.57$

Dissociation: $C_3\bullet CCOOH \rightarrow C{=}C(C_2){+}CH_2O{+}OH$

The high pressure limit rate constant: A factor: 7.6112×10^{14}, n= -1.068, $E_a = 24.00$

Epoxide Fromation, (OH Elimination): $C_3\bullet CCOOH \rightarrow C_2CyCCOC + OH$

Transition state theory and semi-empirical calculations are used to calculate the A factor. Corrections include loss of optical isomer –OOH. Analysis over the T range gives A factor of 3.6937×10^{9}, n= 1.34882, E_a =17.88 kcal.

3.7 Results and Discussion

Transition States of Important Reaction

$C_3CCOO\bullet \rightarrow TS(1) \rightarrow C_3\bullet CCOOH$:

The structure of transition state for isomerization of neopentyl peroxy ($C_3CCOO\bullet$) to neopentyl hydroperoxide (C3•CCOOH) determined by B3LYP/6-31g(d,p) density functional calculation, is shown in Figure 3. The breaking C-H bond stretchs to 1.30 angstroms from 1.09 angstroms, and the forming O-H bond length is 1.292 angstroms which is longer that regular O-H bond length 0.95 angstroms.

Thermodydnamic properties for this transition state, reactant and product have been calculated from B3LYP/6-31g(d,p), B3LYP/6-311+G(3df,2p), and CBS-Q //B3LYP/6-31G(d,p) calculations levels and are listed in Table 16.

$C_3\bullet CCOOH \rightarrow TS(2) \rightarrow C_2C{=}C + CH_2O + OH$:

This study calculates a transition state where a $C\bullet H_2OOH$ or a R-C•HOOH is formed. The calculation shows that, C-O bond in the leaving group, is only slightly decreased in length from 1.394 to 1.345 angstroms.

$C_3\bullet CCOOH \rightarrow TS(3) \rightarrow C{=}C(C_2) + CH_2O + OH$:

Figure 5 shows the structure of the transition state for this reaction. The calculation shows that The $C_3\bullet C$-COOH bond length is increased 1.4114 from 1.4114 to 1.4978 angstroms.

C_3•CCOOH → TS(4) → C_2CyCCOC +OH:

Figure 6 shows the structure of the transition state for this reaction. The breaking O-O bond length is 1.630 angstroms and the forming C-O bond length is 1.866 angstroms; 1.253 and 1.310 times longer than normal RO-O• and R-OO• bond lengths of 1.3008 and 1.4249 angstroms respectively. [46] This reaction is responsible for a major fraction of the OH formation.

C_3CCOO• → TS(5) → C_3CC=O + OH:

The structure of transition state of neopentyl peroxy (C_3CCOO•) to C_3CC=O + OH determined by B3LYP/6-31g(d,p) density functional calculation, is shown in Figure 7. The breaking C-H bond stretchs to 1.284 angstroms from 1.105 angstroms, and the forming O-H bond length is 1.292 angstroms which is longer that regular O-H bond length 0.95 angstroms.

Analysis For Chemical Activation Reactions

C_3CC• + O_2:

An energy level diagram is shown in Figure 18, and data for each high pressure limit rate constant are listed in the Tables 18. Reaction channels for the energized adduct C_3CCOO• include dissociation back to reactant, stabilization to C_3CCOO•, and isomerization via hydrogen transfer. The energized isomer can undergo cyclic ether formation, elimination (beta scission) or stabilization. The barrier for isomerization to C_3•CCOOH is evaluated as 22.88 kcal/mol, which is 10.65 kcal/mol lower than dissociation back to reactants, there is sufficient energy in the adduct C_3CCOO• to allow isomerization to occur before it is stabilized; because isomerization has a low A factor (tight transition state). Fall off at 700k occurs because of energized adduct dissociation (reverse reaction). The important isomer (C_3•CCOOH) product channel is C_3CyCCOC + OH, and next important product channels are $C_2C=C$ + CH_2O + OH and C=C(C)COOH + CH_3. Subsequent reactions of this stabilized isomer (C_3•CCOOH) with O_2 will also be important at conditions where stabilization occurs and O_2 is present. The channel to $C_3CC=O$ +OH (endothermic, beta scission of the C_3CC•OOH) also has some significance. Input parameters to the calculation and the calculated rate constants are listed in Tables 18 and 19. Figure 19 shows the apparent rate constants for the product channels of C_3CC• + O_2 versus temperature from 300 to 1300 k. results are shown at 1 atm. Figure 18 show that the dominant product channel for C_3CC• + O_2 is stabilization to C_3CCOO• below 700 k. A fraction (approximately 10 % at 1.0 atm) of the chemically activated C_3CCOO• directly reacts to products via the isomerization. This is responsible for formation of some of major product C_3CyCCOC + OH.

Figure 20 illustrates the pressure dependence for the rate constants of the chemically activated reactions. Stabilization to C_3CCOO• is the dominant product channel over almost all pressures. Other product channels decrease relative to stabilization as the pressure increases.

Fate of Stabilized Adducts - Dissociation Reactions

The computed results for the rate of O_2 addition to neopentyl radical shows that the main product path is stabilization for almost all pressures. It is, therefore, important to determine the fate of the stabilized peroxy adduct as function of temperature.

C_3CCOO•:

There are two important reactions of stabilized C_3CCOO• at atmospheric pressure. Isomerization via a H atom shift followed by a beta scission to a cyclic ether + OH when temperature is below 700k. The formation of $C_2CyCCOC$ is from this path. At temperature of 700 K, dissociation back to reactants $C_3CC\bullet + O_2$ is the dominant channel for stabilized peroxy radical in the pressure range up to 1 atm. The isomerization channel is, however, competitive; but the $C_3\bullet CCOOH$ isomer rapidly reacts back to $C_3CCOO\bullet$ with a barrier of only 10.65 kcal/mol.

$C_3\bullet CCOOH$:

The dominant unimolecular reaction of $C_3\bullet CCOOH$ is reverse isomerization with 1 % to epoxide + OH. This results in a near equilibrium with neopentyl radical $C_3CCOO\bullet$ and a slow (bleed) reaction to epoxide + OH products.

OH Formation

The OH radical is generated by three major paths: (i) Dissociation of hydroperoxy alkyl isomer to OH + a cyclic; (ii) Dissociation of $C_3\bullet CCOOH$ to $C_2C{=}C + CH_2O + OH$; (iii) Dissociation of $C_3CCOO\bullet$ to $C_3CC{=}C + CH_2O + OH$. Figure 18 shows how reaction paths generate OH radical. Figure 23 shows that the slope of concentration of OH depends on time.

The hydrogen shift in these isomers is facilitated via hydrogen bonding between the peroxy oxygen radical and the OH group and will be discussed further in a future paper on stable product formation in neopentyl oxidation.

CHAPTER 4

CONCLUSIONS

Thermodynamic properties of vinyl alcohol and methyl vinyl ether and related radicals corresponding to loss of H atom for a carbon are calculated using density functional and ab initio methods with isodesmic working reactions schemes for cancellation of errors. Standard enthalpies of formation, $\Delta H°_{f\,298}$ are calculated based on the B3LYP/6-31g(d,p), B3LYP/6-311+G(3df,2p), ab initio QCISD(T)/6-31g(d,p), and CBS-Q//B3LYP/6-31G(d,p) levels and include the statistical distribution of rotational conformers. Entropies ($S°_{298}$) and heat capacity ($C_p(T)$, $10 \leq T/K \leq 5000$) are determined with optimized geometries and frequencies. Hindered internal rotation contributions to entropy and heat capacity are calculated by intramolecular torsion potential curves, and the entropy correction for mixing of rotation.

The value of $O/C_D/H$ and $O/C/C_D$ group (for group additivity) are –44.57 and –29.80 kcal/mol and the anti group of $O/C_D/H$ and $O/C/C_D$ group (for group additivity) are – 44.42 and –29.69 kcal/mol. These require use of $C_D/H/O$ group enthalpy value of 8.60 kcal/mol.

Bond energies on vinyl alcohols and ethers are: The $\Delta H°_{f\,298}$ value of H---CH=CHOH (114.15 kcal/mol), CH_2=C(OH)---H (108.18), CH_2=CHO---H (85.74), H---CH=$CHOCH_3$ (114.06), CH_2=$C(OCH_3)$---H (109.31), CH_2=$CHOCH_2$---H (98.96).

This study calculated thermodynamic properties, transition state structure and energy, and developed a mechanism describing reaction paths and kinetic parameters for the neopentyl radical + oxygen reaction system, the sub-system of neopentyl peroxy and the radical isomer isomer: neopentyl hydroperoxide radical + O_2 reaction system. Transition states for several important reactions – isomerization of neopentyl peroxy radical, the formation of cyclic ether and elimination(β - scission) of the hydroperoxide – alkyl radical isomer are illustrated. This study evaluates barriers to isomerization and epoxide formation reactions as 23.53 and 17.23 kcal /mol, respectively.

APPENDIX A
VINYL ALCOHOL AND ETHER

Tables and Figures explain all the aspects of vinyl alcohol and ether.

Table A.1 Geometry Parameters for syn and anti CH_2=CHOH

Anti CH_2=CHOH			Syn CH_2=CHOH		
Name	Definition	Value	Name	Definition	Value
R1	R(1,2)	1.331	R1	R(1,2)	1.334
R2	R(1,5)	1.083	R2	R(1,4)	1.083
R3	R(1,6)	1.084	R3	R(1,5)	1.087
R4	R(2,3)	1.369	R4	R(2,3)	1.362
R5	R(2,7)	1.090	R5	R(2,6)	1.086
R6	R(3,4)	0.964	R6	R(3,7)	0.968
A1	A(2,1,5)	120.012	A1	A(2,1,4)	120.159
A2	A(2,1,6)	121.390	A2	A(2,1,5)	122.288
A3	A(5,1,6)	118.598	A3	A(4,1,5)	117.553
A4	A(1,2,3)	122.400	A4	A(1,2,3)	127.174
A5	A(1,2,7)	121.754	A5	A(1,2,6)	122.518
A6	A(3,2,7)	115.846	A6	A(3,2,6)	110.309
A7	A(2,3,4)	109.096	A7	A(2,3,7)	108.723
D1	D(5,1,2,3)	179.859	D1	D(4,1,2,3)	180.000
D2	D(5,1,2,7)	-0.040	D2	D(4,1,2,6)	0.000
D3	D(6,1,2,3)	-0.096	D3	D(5,1,2,3)	0.000
D4	D(6,1,2,7)	-179.995	D4	D(5,1,2,6)	-180.000
D5	D(1,2,3,4)	179.321	D5	D(1,2,3,7)	-0.002
D6	D(7,2,3,4)	-0.775	D6	D(6,2,3,7)	179.998

Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level. Bond length or the distance between two atoms of number in Å . Bond angel or the angle among three atoms of number in degree.

Table A.2 Geometry Parameters for syn and anti C·H=CHOH

Anti C·H=CHOH			Syn C·H=CHOH		
Name	Definition	Value	Name	Definition	Value
R1	R(1,2)	1.315	R1	R(1,2)	1.315
R2	R(1,3)	1.078	R2	R(1,3)	1.079
R3	R(2,4)	1.091	R3	R(2,4)	1.088
R4	R(2,5)	1.380	R4	R(2,5)	1.378
R5	R(5,6)	0.965	R5	R(5,6)	0.968
A1	A(1,2,4)	120.361	A1	A(1,2,4)	122.056
A2	A(1,2,5)	124.021	A2	A(1,2,5)	127.946
A3	A(4,2,5)	115.618	A3	A(4,2,5)	109.998
A4	A(2,5,6)	108.370	A4	A(2,5,6)	108.505
A5	L(2,1,3,5,-1)	141.080	A5	L(2,1,3,5,-1)	141.682
A6	L(2,1,3,5,-2)	180.001	A6	L(2,1,3,5,-2)	180.037
D1	D(1,2,5,6)	-179.977	D1	D(1,2,5,6)	0.013
D2	D(4,2,5,6)	0.026	D2	D(4,2,5,6)	-179.999

Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level. Bond length or the distance between two atoms of number in Å . Bond angel or the angle among three atoms of number in degree.

Table A.3 Geometry Parameters for syn CH_2=C·OH and anti CH_2=C·OH

Anti CH_2=C·OH			Syn CH_2=C·OH		
Name	Definition	Value	Name	Definition	Value
R1	R(2,1)	1.322	R1	R(2,1)	1.322
R2	R(3,1)	1.083	R2	R(3,1)	1.085
R3	R(4,1)	1.090	R3	R(4,1)	1.085
R4	R(5,2)	1.340	R4	R(5,2)	1.342
R5	R(6,5)	0.968	R5	R(6,5)	0.954
A1	A(2,1,3)	120.535	A1	A(2,1,3)	118.984
A2	A(2,1,4)	121.279	A2	A(2,1,4)	125.22
A3	A(3,1,4)	118.174	A3	A(3,1,4)	115.765
A4	A(1,2,5)	130.334	A4	A(1,2,5)	149.612
A5	A(2,5,6)	109.396	A5	A(2,5,6)	109.101
D1	D(5,2,1,3)	171.101	D1	D(5,2,1,3)	-175.689
D2	D(5,2,1,4)	-10.151	D2	D(5,2,1,4)	6.445
D3	D(6,5,2,1)	140.534	D3	D(6,5,2,1)	26.167

Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level. Bond length or the distance between two atoms of number in Å . Bond angel or the angle among three atoms of number in degree.

Table A.4 Geometry Parameters for anti CH_2=$CHOCH_3$ and syn CH_2=$CHOCH_3$

Anti CH_2=$CHOCH_3$			Syn CH_2=$CHOCH_3$		
Name	Definition	Value	Name	Definition	Value
R1	R(1,2)	1.332	R1	R(2,1)	1.336
R2	R(1,5)	1.083	R2	R(3,2)	1.358
R3	R(1,6)	1.084	R3	R(4,3)	1.420
R4	R(2,3)	1.363	R4	R(5,1)	1.083
R5	R(2,7)	1.091	R5	R(6,1)	1.083
R6	R(3,4)	1.420	R6	R(7,2)	1.087
R7	R(4,8)	1.098	R7	R(8,4)	1.098
R8	R(4,9)	1.098	R8	R(9,4)	1.098
R9	R(4,10)	1.091	R9	R(10,4)	1.091
A1	A(2,1,5)	119.888	A1	A(1,2,3)	128.423
A2	A(2,1,6)	121.411	A2	A(2,3,4)	116.652
A3	A(5,1,6)	118.702	A3	A(2,1,5)	118.895
A4	A(1,2,3)	122.472	A4	A(2,1,6)	123.694
A5	A(1,2,7)	122.084	A5	A(5,1,6)	117.411
A6	A(3,2,7)	115.443	A6	A(1,2,7)	121.945
A7	A(2,3,4)	115.366	A7	A(3,2,7)	109.632
A8	A(3,4,8)	111.624	A8	A(3,4,8)	111.198
A9	A(3,4,9)	111.610	A9	A(3,4,9)	111.198
A10	A(3,4,10)	106.680	A10	A(8,4,9)	108.847
A11	A(8,4,9)	108.970	A11	A(3,4,10)	106.425
A12	A(8,4,10)	108.944	A12	A(8,4,10)	109.569
A13	A(9,4,10)	108.929	A13	A(9,4,10)	109.569
D1	D(5,1,2,3)	-179.610	D1	D(3,2,1,5)	180.000
D2	D(5,1,2,7)	0.143	D2	D(3,2,1,6)	0.000
D3	D(6,1,2,3)	0.266	D3	D(7,2,1,5)	0.000
D4	D(6,1,2,7)	-179.981	D4	D(7,2,1,6)	180.000
D5	D(1,2,3,4)	-178.176	D5	D(4,3,2,1)	-0.003
D6	D(7,2,3,4)	2.056	D6	D(4,3,2,7)	179.997
D7	D(2,3,4,8)	62.134	D7	D(8,4,3,2)	-60.730
D8	D(2,3,4,9)	-60.085	D8	D(9,4,3,2)	60.739
D9	D(2,3,4,10)	-178.963	D9	D(10,4,3,2)	-179.995

Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level.Bond length or the distance between two atoms of number in Å .Bond angel or the angle among three atoms of number in degree.

Table A.5 Geometry Parameters for anti $CH_2=CHOCH_3$ and syn $C\cdot H=CHOCH_3$

Anti $C\cdot H=CHOCH_3$			Syn $C\cdot H=CHOCH_3$		
Name	Definition	alue	Name	Definition	Value
R1	R(1,2)	1.316	R1	R(1,2)	1.318
R2	R(1,5)	1.078	R2	R(1,5)	1.077
R3	R(2,3)	1.374	R3	R(2,3)	1.371
R4	R(2,6)	1.092	R4	R(2,6)	1.088
R5	R(3,4)	1.423	R5	R(3,4)	1.422
R6	R(4,7)	1.098	R6	R(4,7)	1.098
R7	R(4,8)	1.098	R7	R(4,8)	1.098
R8	R(4,9)	1.091	R8	R(4,9)	1.091
A1	A(1,2,3)	123.995	A1	A(1,2,3)	128.603
A2	A(1,2,6)	120.666	A2	A(1,2,6)	121.653
A3	A(3,2,6)	115.339	A3	A(3,2,6)	109.744
A4	A(2,3,4)	114.757	A4	A(2,3,4)	115.488
A5	A(3,4,7)	111.622	A5	A(3,4,7)	111.098
A6	A(3,4,8)	111.622	A6	A(3,4,8)	111.097
A7	A(3,4,9)	106.421	A7	A(3,4,9)	106.476
A8	A(7,4,8)	109.057	A8	A(7,4,8)	108.819
A9	A(7,4,9)	109.017	A9	A(7,4,9)	109.659
A10	A(8,4,9)	109.016	A10	A(8,4,9)	109.663
A11	L(2,1,5,3,-1)	140.637	A11	L(2,1,5,3,-1)	142.794
A12	L(2,1,5,3,-2)	179.990	A12	L(2,1,5,3,-2)	180.029
D1	D(1,2,3,4)	-179.931	D1	D(1,2,3,4)	0.044
D2	D(6,2,3,4)	0.048	D2	D(6,2,3,4)	-179.959
D3	D(2,3,4,7)	61.218	D3	D(2,3,4,7)	-60.717
D4	D(2,3,4,8)	-61.121	D4	D(2,3,4,8)	60.578
D5	D(2,3,4,9)	-179.951	D5	D(2,3,4,9)	179.932

Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level. Bond length or the distance between two atoms of number in Å. Bond angel or the angle among three atoms of number in degree.

Table A.6 Geometry Parameters for syn $CH_2{=}C{\cdot}OCH_3$ and anti $CH_2{=}C{\cdot}OCH_3$

Anti $CH_2{=}C{\cdot}OCH_3$			Syn $CH2{=}C{\cdot}OCH_3$		
Name	Definition	Value	Name	Definition	Value
R1	R(2,1)	1.323	R1	R(2,1)	1.324
R2	R(3,2)	1.331	R2	R(3,2)	1.316
R3	R(4,3)	1.437	R3	R(4,3)	1.445
R4	R(5,1)	1.084	R4	R(5,1)	1.083
R5	R(6,1)	1.091	R5	R(6,1)	1.091
R6	R(7,4)	1.090	R6	R(7,4)	1.089
R7	R(8,4)	1.095	R7	R(8,4)	1.095
R8	R(9,4)	1.094	R8	R(9,4)	1.095
A1	A(1,2,3)	130.334	A1	A(1,2,3)	137.286
A2	A(2,3,4)	115.631	A2	A(2,3,4)	116.805
A3	A(2,1,5)	120.568	A3	A(2,1,5)	120.517
A4	A(2,1,6)	121.371	A4	A(2,1,6)	122.074
A5	A(5,1,6)	118.059	A5	A(5,1,6)	117.410
A6	A(3,4,7)	106.238	A6	A(3,4,7)	106.154
A7	A(3,4,8)	110.530	A7	A(3,4,8)	110.045
A8	A(7,4,8)	110.018	A8	A(7,4,8)	110.378
A9	A(3,4,9)	110.541	A9	A(3,4,9)	110.044
A10	A(7,4,9)	109.953	A10	A(7,4,9)	110.391
A11	A(8,4,9)	109.518	A11	A(8,4,9)	109.775
D1	D(3,2,1,5)	-171.790	D1	D(3,2,1,5)	-179.952
D2	D(3,2,1,6)	8.732	D2	D(3,2,1,6)	0.068
D3	D(4,3,2,1)	-132.710	D3	D(4,3,2,1)	0.194
D4	D(7,4,3,2)	-179.146	D4	D(7,4,3,2)	179.910
D5	D(8,4,3,2)	61.528	D5	D(8,4,3,2)	-60.645
D6	D(9,4,3,2)	-59.892	D6	D(9,4,3,2)	60.451

Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level. Bond length or the distance between two atoms of number in Å . Bond angel or the angle among three atoms of number in degree.

Table A.7 Geometry Parameters[a] for of syn $CH_2{=}CHOC{\cdot}H_2$ and anti $CH_2{=}CHOC{\cdot}H_2$

Anti $CH_2{=}CHOC{\cdot}H_2$			Syn $CH_2{=}CHOC{\cdot}H_2$		
Name	Definition	Value	Name	Definition	Value
R1	R(1,2)	1.332	R1	R(1,2)	1.334
R2	R(1,5)	1.082	R2	R(1,5)	1.083
R3	R(1,6)	1.084	R3	R(1,6)	1.083
R4	R(2,3)	1.367	R4	R(2,3)	1.369
R5	R(2,7)	1.089	R5	R(2,7)	1.085
R6	R(3,4)	1.364	R6	R(3,4)	1.362
R7	R(4,8)	1.081	R7	R(4,8)	1.082
R8	R(4,9)	1.087	R8	R(4,9)	1.086
A1	A(2,1,5)	119.794	A1	A(2,1,5)	119.026
A2	A(2,1,6)	121.446	A2	A(2,1,6)	123.021
A3	A(5,1,6)	118.761	A3	A(5,1,6)	117.932
A4	A(1,2,3)	121.585	A4	A(1,2,3)	127.251
A5	A(1,2,7)	123.323	A5	A(1,2,7)	123.107
A6	A(3,2,7)	115.092	A6	A(3,2,7)	109.638
A7	A(2,3,4)	118.662	A7	A(2,3,4)	119.563
A8	A(3,4,8)	113.067	A8	A(3,4,8)	112.636
A9	A(3,4,9)	118.047	A9	A(3,4,9)	117.828
A10	A(8,4,9)	121.598	A10	A(8,4,9)	121.603
D1	D(5,1,2,3)	-179.473	D1	D(5,1,2,3)	-179.533
D2	D(5,1,2,7)	0.378	D2	D(5,1,2,7)	1.216
D3	D(6,1,2,3)	0.495	D3	D(6,1,2,3)	2.163
D4	D(6,1,2,7)	-179.654	D4	D(6,1,2,7)	-177.088
D5	D(1,2,3,4)	-177.691	D5	D(1,2,3,4)	13.201
D6	D(7,2,3,4)	2.446	D6	D(7,2,3,4)	-167.466
D7	D(2,3,4,8)	-171.121	D7	D(2,3,4,8)	-177.075
D8	D(2,3,4,9)	-20.412	D8	D(2,3,4,9)	33.369

Geometry is optimized in B3LYP/6-31g(d,p) density functional calculation level. Bond length or the distance between two atoms of number in Å. Bond angel or the angle among three atoms of number in degree.

Table A.8 Total Energy and Internal Rotation Barriers CH_2=CH---OH

CH_2=CH---OH			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-153.816	0	0
15	-153.815	0.00057	0.357681
30	-153.814	0.00229	1.436998
45	-153.811	0.0047	2.949297
60	-153.809	0.00708	4.442771
75	-153.807	0.00872	5.471887
90	-153.807	0.00918	5.760542
105	-153.808	0.00849	5.32756
120	-153.809	0.00709	4.449046
135	-153.811	0.00553	3.47013
150	-153.812	0.00428	2.685743
165	-153.813	0.00353	2.21511
180	-153.813	0.00328	2.058233
195	-153.813	0.00347	2.17746
210	-153.812	0.00415	2.604166
225	-153.811	0.00534	3.350903
240	-153.809	0.00688	4.317269
255	-153.808	0.00834	5.233433
270	-153.807	0.00915	5.741716
285	-153.807	0.00886	5.559739
300	-153.809	0.00736	4.618474
315	-153.811	0.00503	3.156375
330	-153.813	0.00259	1.625251
345	-153.815	0.00074	0.464357
360	-153.816	0	0

Table A.9 Total Energy and Internal Rotation Barriers C·H=CH---OH

C·H=CH---OH			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-153.123	0	0
15	-153.122	0.00057	0.357681
30	-153.121	0.00214	1.342871
45	-153.119	0.0043	2.698293
60	-153.116	0.00641	4.022339
75	-153.115	0.00781	4.900853
90	-153.115	0.00819	5.139307
105	-153.115	0.00765	4.800451
120	-153.116	0.00659	4.135291
135	-153.117	0.00545	3.419929
150	-153.118	0.00455	2.85517
165	-153.119	0.00403	2.528865
180	-153.119	0.00387	2.428464
195	-153.119	0.00403	2.528865
210	-153.118	0.00455	2.85517
225	-153.117	0.00545	3.419929
240	-153.116	0.0066	4.141566
255	-153.115	0.00765	4.800451
270	-153.115	0.00819	5.139307
285	-153.115	0.00781	4.900853
300	-153.117	0.0064	4.016064
315	-153.119	0.00429	2.692018
330	-153.121	0.00213	1.336596
345	-153.122	0.00056	0.351406
360	-153.123	0	0

Table A.10 Total Energy and Internal Rotation Barriers $CH_2=C\cdot$ ---OH

$CH_2=C\cdot$ ---OH			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-153.133	0	0
15	-153.132	0.0004	0.251004
30	-153.131	0.0013	0.815763
45	-153.131	0.00147	0.92244
60	-153.132	0.00059	0.370231
75	-153.133	2E-05	0.01255
90	-153.132	0.0002	0.125502
105	-153.132	0.00094	0.589859
120	-153.131	0.00186	1.167169
135	-153.13	0.00263	1.650351
150	-153.13	0.00306	1.920181
165	-153.129	0.0032	2.008032
180	-153.129	0.0033	2.070783
195	-153.129	0.00359	2.252761
210	-153.129	0.00404	2.53514
225	-153.129	0.00411	2.579066
240	-153.129	0.00369	2.315512
255	-153.129	0.00334	2.095883
270	-153.129	0.00322	2.020582
285	-153.13	0.00311	1.951556
300	-153.13	0.00276	1.731928
315	-153.131	0.00206	1.292671
330	-153.131	0.00115	0.721636
345	-153.132	0.00034	0.213353
360	-153.133	0	0

Table A.11 Total Energy and Internal Rotation Barriers CH_2=CHO---CH_3

CH_2=CHO---CH_3			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-193.11929	0	0
15	-193.11915	0.00014	0.0878514
30	-193.11857	0.00072	0.4518072
45	-193.11792	0.00137	0.8596887
60	-193.11768	0.00161	1.0102911
75	-193.11804	0.00125	0.7843875
90	-193.11872	0.00057	0.3576807
105	-193.11922	7E-05	0.0439257
120	-193.11929	0	0
135	-193.11912	0.00017	0.1066767
150	-193.11854	0.00075	0.4706325
165	-193.11791	0.00138	0.8659638
180	-193.11768	0.00161	1.0102911
195	-193.118	0.00129	0.8094879
210	-193.11865	0.00064	0.4016064
225	-193.11918	0.00011	0.0690261
240	-193.11929	0	0
255	-193.11917	0.00012	0.0753012
270	-193.11861	0.00068	0.4267068
285	-193.11795	0.00134	0.8408634
300	-193.11768	0.00161	1.0102911
315	-193.11801	0.00128	0.8032128
330	-193.11868	0.00061	0.3827811
345	-193.1192	9E-05	0.0564759
360	-193.11929	0	0

Table A.12 Total Energy and Internal Rotation Barriers CH_2=CH---OCH_3

CH_2=CH---OCH_3			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-193.123	0	0
15	-193.122	0.00105	0.658885
30	-193.119	0.00356	2.233936
45	-193.116	0.00673	4.223142
60	-193.114	0.00921	5.779367
75	-193.113	0.00997	6.256275
90	-193.114	0.00934	5.860943
105	-193.115	0.00785	4.925953
120	-193.117	0.00611	3.834086
135	-193.118	0.00467	2.930472
150	-193.119	0.00382	2.397088
165	-193.119	0.00355	2.22766
180	-193.119	0.00355	2.22766
195	-193.119	0.00357	2.240211
210	-193.119	0.00394	2.472389
225	-193.118	0.00492	3.087349
240	-193.116	0.00644	4.041164
255	-193.115	0.00819	5.139307
270	-193.113	0.00956	5.998996
285	-193.113	0.00995	6.243725
300	-193.114	0.00883	5.540913
315	-193.117	0.00609	3.821536
330	-193.12	0.00296	1.85743
345	-193.122	0.0007	0.439257
360	-193.123	0	0

Table A.13 Total Energy and Internal Rotation Barriers CH_2=C·O---CH_3

CH_2=C·O---CH_3			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-192.43946	0	0
15	-192.43923	0.00023	0.1443273
30	-192.43866	0.0008	0.502008
45	-192.43809	0.00137	0.8596887
60	-192.43783	0.00163	1.0228413
75	-192.43806	0.0014	0.878514
90	-192.43865	0.00081	0.5082831
105	-192.43923	0.00023	0.1443273
120	-192.43946	0	0
135	-192.43922	0.00024	0.1506024
150	-192.43866	0.0008	0.502008
165	-192.4381	0.00136	0.8534136
180	-192.43783	0.00163	1.0228413
195	-192.43803	0.00143	0.8973393
210	-192.43858	0.00088	0.5522088
225	-192.43918	0.00028	0.1757028
240	-192.43946	0	0
255	-192.43925	0.00021	0.1317771
270	-192.4387	0.00076	0.4769076
285	-192.43812	0.00134	0.8408634
300	-192.43783	0.00163	1.0228413
315	-192.43802	0.00144	0.9036144
330	-192.43859	0.00087	0.5459337
345	-192.4392	0.00026	0.1631526
360	-192.43946	0	0

Table A.14 Total Energy and Internal Rotation Barriers $CH_2{=}C\cdot$ --- OCH_3

$CH_2{=}C\cdot$ --- OCH_3			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-192.439	0	0
15	-192.439	0.00038	0.238454
30	-192.438	0.0014	0.878514
45	-192.437	0.00231	1.449548
60	-192.438	0.00169	1.060492
75	-192.439	0.00057	0.357681
90	-192.439	3E-05	0.018825
105	-192.439	0.00017	0.106677
120	-192.439	0.00078	0.489458
135	-192.438	0.0016	1.004016
150	-192.437	0.00235	1.474649
165	-192.437	0.00281	1.763303
180	-192.437	0.00277	1.738203
195	-192.437	0.00255	1.60015
210	-192.437	0.00253	1.5876
225	-192.437	0.00265	1.662901
240	-192.437	0.00256	1.606426
255	-192.437	0.00252	1.581325
270	-192.437	0.00271	1.700552
285	-192.437	0.00285	1.788403
300	-192.437	0.0025	1.568775
315	-192.438	0.00179	1.123243
330	-192.439	0.00096	0.60241
345	-192.439	0.00028	0.175703
360	-192.439	0	0

Table A.15 Total Energy and Internal Rotation Barriers $CH_2=CHO{-}{-}{-}C{\cdot}H_2$

$CH_2=CHO{-}{-}{-}C{\cdot}H_2$			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-192.455	0	0
15	-192.455	0.00049	0.30748
30	-192.455	0.00037	0.232179
45	-192.453	0.00168	1.054217
60	-192.451	0.00382	2.397088
75	-192.449	0.00649	4.07254
90	-192.446	0.00901	5.653865
105	-192.448	0.00706	4.430221
120	-192.451	0.00425	2.666918
135	-192.453	0.0019	1.192269
150	-192.455	0.00049	0.30748
165	-192.455	0	0
180	-192.455	0.00022	0.138052
195	-192.455	0.00022	0.138052
210	-192.455	0	0
225	-192.455	0.00049	0.30748
240	-192.453	0.0019	1.192269
255	-192.451	0.00425	2.666918
270	-192.448	0.00706	4.430221
285	-192.446	0.00901	5.653865
300	-192.449	0.00649	4.07254
315	-192.451	0.00382	2.397088
330	-192.453	0.00168	1.054217
345	-192.455	0.00037	0.232179
360	-192.455	0	0

Table A.16 Total Energy and Internal Rotation Barriers $CH_2{=}CH{-}{-}{-}OC{\cdot}H_2$

$CH_2{=}CH{-}{-}{-}OC{\cdot}H_2$			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-192.456	0	0
15	-192.455	0.00058	0.363956
30	-192.456	2E-05	0.01255
45	-192.455	0.00103	0.646335
60	-192.452	0.0032	2.008032
75	-192.45	0.0056	3.514056
90	-192.449	0.00717	4.499247
105	-192.448	0.00736	4.618474
120	-192.449	0.00634	3.978413
135	-192.451	0.00466	2.924197
150	-192.453	0.00293	1.838604
165	-192.454	0.00156	0.978916
180	-192.455	0.00079	0.495733
195	-192.455	0.00062	0.389056
210	-192.455	0.00085	0.533384
225	-192.454	0.0017	1.066767
240	-192.453	0.00313	1.964106
255	-192.451	0.00488	3.062249
270	-192.449	0.00652	4.091365
285	-192.448	0.00741	4.649849
300	-192.449	0.00705	4.423945
315	-192.45	0.00534	3.350903
330	-192.453	0.00291	1.826054
345	-192.455	0.00084	0.527108
360	-192.456	0	0

Table A.17 Total Energy and Internal Rotation Barriers C·H=CHO---CH$_3$

C·H=CHO---CH$_3$			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-192.426	0	0
15	-192.425	2E-05	0.01255
30	-192.425	0.00059	0.370231
45	-192.424	0.00137	0.859689
60	-192.424	0.00174	1.091867
75	-192.424	0.0014	0.878514
90	-192.425	0.00062	0.389056
105	-192.425	3E-05	0.018825
120	-192.425	6E-05	0.037651
135	-192.425	3E-05	0.018825
150	-192.425	0.00063	0.395331
165	-192.424	0.00141	0.884789
180	-192.424	0.00174	1.091867
195	-192.424	0.00136	0.853414
210	-192.425	0.00058	0.363956
225	-192.426	1E-05	0.006275
240	-192.425	5E-05	0.031376
255	-192.425	6E-05	0.037651
270	-192.425	0.00067	0.420432
285	-192.424	0.00141	0.884789
300	-192.424	0.00174	1.091867
315	-192.424	0.0014	0.878514
330	-192.425	0.00066	0.414157
345	-192.425	5E-05	0.031376
360	-192.426	0	0

Table A.18 Total Energy and Internal Rotation Barriers C·H=CH---OCH_3

C·H=CH---OCH_3			
Torsion Angle	Total E(hartree)	Rotational barrier	E(kcal/mole)
0	-192.43	0	0
15	-192.429	0.00084	0.527108
30	-192.427	0.00309	1.939006
45	-192.424	0.00601	3.771335
60	-192.422	0.00844	5.296184
75	-192.421	0.00937	5.879769
90	-192.421	0.00886	5.559739
105	-192.423	0.00761	4.775351
120	-192.424	0.00624	3.915662
135	-192.425	0.0052	3.263052
150	-192.426	0.00468	2.936747
165	-192.426	0.00464	2.911646
180	-192.425	0.00473	2.968122
195	-192.426	0.00464	2.911646
210	-192.426	0.00468	2.936747
225	-192.425	0.0052	3.263052
240	-192.424	0.00624	3.915662
255	-192.423	0.00761	4.775351
270	-192.421	0.00886	5.559739
285	-192.421	0.00937	5.879769
300	-192.422	0.00844	5.296184
315	-192.424	0.006	3.76506
330	-192.427	0.00309	1.939006
345	-192.429	0.00084	0.527108
360	-192.43	0	0

Table A.19 Total Energy, ZPVE, and Thermal Correction for Standard Species used in Reaction Schemes and Bond Energy Calculations

Species	**ZPVE**[a]	**Thermal.**	**Total Energy**			**CBS-Q(298)** [f]
		corr[b].	B3LYP/6-31[c]	B3LYP/6-311[d]	Qcisd(t)[e]	
CH_4	0.04502	0.003811	-40.476	-40.488	-40.342	-40.405
CH_3OH	0.05141	0.004245	-115.557	-115.563	-115.498	-115.534
$CH_3CH_2CH_3$	0.10369	0.005468	-118.875	-118.881	-118.814	-118.849
C_2H_5OH	0.05629	0.004813	-154.789	-154.791	-154.726	-154.763
C_2H_6	0.07492	0.004422	-79.659	-79.664	-79.595	-79.625
CH_3OCH_3	0.07991	0.005249	-154.786	-154.792	-154.704	-154.745
$CH_2=CH_2$	0.05112	0.003987	-78.437	-78.441	-78.396	-78.411
$CH_2=CHCH_3$	0.07983	0.00503	-117.653	-117.673	-117.613	-117.640
$CH_3C{\cdot}HOH$	0.08015	0.005221	-154.150	-154.157	-154.102	-154.120
$C{\cdot}H=CH_2$	0.03663	0.004043	-77.774	-77.783	-77.726	-77.743
$CH_3CH_2OCH_3$	0.08579	0.005674	-193.994	-194.000	-193.947	-193.973
$CH_2=CHO{\cdot}$	0.04260	0.004464	-152.957	-152.965	-152.913	-152.926

[a] ZPVE : scaled zero-point energies in Hartree (scaled by 0.9806) [b] Therm. corr. : Thermal corrections in Hartree. [c] B3lyp/6-31G(d,p). Total energies are in Hartree at 0 K. [d] B3lyp/6-311+G(3df,2p). [e] QCISD(T)/6-31G(d,p). [f] CBS-Q enthalpies are in Hartree, which include thermal correction and zero point energy at 298.15 K.

APPENDIX B
NEOPENTY MOLECULE

Tables and Figures explain the structure and all the properties of neopentyl and radicals.

Table B.1 Geometry Parameters for $C_3CCOO\bullet$

$C_3CCOO\bullet$					
Definition	Value	Definition	Value	Definition	Value
R(1,2)	1.53	A(2,3,14)	111.8455	D(1,2,3,15)	60.4673
R(1,8)	1.0984	A(2,3,15)	111.3662	D(1,2,3,16)	-59.3492
R(1,9)	1.0981	A(2,3,16)	110.9303	D(4,2,3,14)	-59.3753
R(1,10)	1.0983	A(14,3,15)	107.6726	D(4,2,3,15)	-179.9084
R(2,3)	1.5262	A(14,3,16)	107.2148	D(4,2,3,16)	60.275
R(2,4)	1.5263	A(15,3,16)	107.5986	D(5,2,3,14)	63.3254
R(2,5)	1.5397	A(2,4,11)	111.8624	D(5,2,3,15)	-57.2077
R(3,14)	1.0978	A(2,4,12)	110.9097	D(5,2,3,16)	-177.0242
R(3,15)	1.0981	A(2,4,13)	111.3551	D(1,2,4,11)	178.9434
R(3,16)	1.0984	A(11,4,12)	107.2212	D(1,2,4,12)	59.2877
R(4,11)	1.0978	A(11,4,13)	107.755	D(1,2,4,13)	-60.414
R(4,12)	1.0984	A(12,4,13)	107.5244	D(3,2,4,11)	59.3399
R(4,13)	1.0981	A(2,5,6)	108.6951	D(3,2,4,12)	-60.3158
R(5,6)	1.4658	A(2,5,17)	110.8744	D(3,2,4,13)	179.9826
R(5,17)	1.1059	A(2,5,18)	110.9863	D(5,2,4,11)	-63.3608
R(5,18)	1.105	A(6,5,17)	109.8012	D(5,2,4,12)	176.9835
R(6,7)	1.2533	A(6,5,18)	108.1864	D(5,2,4,13)	57.2819
A(2,1,8)	111.567	A(17,5,18)	108.2548	D(1,2,5,6)	-179.8104
A(2,1,9)	111.0598	A(5,6,7)	113.8024	D(1,2,5,17)	59.4063
A(2,1,10)	111.533	D(8,1,2,3)	179.7002	D(1,2,5,18)	-60.9482
A(8,1,9)	107.4036	D(8,1,2,4)	59.6494	D(3,2,5,6)	-60.9103
A(8,1,10)	107.6313	D(8,1,2,5)	-60.3347	D(3,2,5,17)	178.3063
A(9,1,10)	107.4329	D(9,1,2,3)	59.9092	D(3,2,5,18)	57.9519
A(1,2,3)	109.12	D(9,1,2,4)	-60.1416	D(4,2,5,6)	61.2484
A(1,2,4)	109.1541	D(9,1,2,5)	179.8743	D(4,2,5,17)	-59.535
A(1,2,5)	107.1045	D(10,1,2,3)	-59.896	D(4,2,5,18)	-179.8895
A(3,2,4)	109.8451	D(10,1,2,4)	-179.9469	D(2,5,6,7)	-171.5795
A(3,2,5)	110.7756	D(10,1,2,5)	60.069	D(17,5,6,7)	-50.137
A(4,2,5)	110.7756	D(1,2,3,14)	-178.9996	D(18,5,6,7)	67.814

Table B.2 Geometry Parameters for C_3•CCOOH

C_3•CCOOH					
Definition	Value	Definition	Value	Definition	Value
R(1,2)	1.5297	A(4,2,5)	111.2572	D(1,2,3,12)	-147.0712
R(1,8)	1.0982	A(2,3,11)	120.8401	D(4,2,3,11)	154.6974
R(1,9)	1.098	A(2,3,12)	121.1131	D(4,2,3,12)	-27.1898
R(1,10)	1.0978	A(11,3,12)	118.0209	D(5,2,3,11)	-82.8576
R(2,3)	1.4852	A(2,4,13)	110.9233	D(5,2,3,12)	95.2553
R(2,4)	1.5269	A(2,4,14)	111.2687	D(1,2,4,13)	58.6914
R(2,5)	1.5455	A(2,4,15)	111.8029	D(1,2,4,14)	-61.1251
R(3,11)	1.0814	A(13,4,14)	107.6536	D(1,2,4,15)	178.537
R(3,12)	1.0812	A(13,4,15)	107.395	D(3,2,4,13)	-61.4354
R(4,13)	1.098	A(14,4,15)	107.596	D(3,2,4,14)	178.7481
R(4,14)	1.098	A(2,5,6)	108.56	D(3,2,4,15)	58.4101
R(4,15)	1.0978	A(2,5,16)	110.19	D(5,2,4,13)	177.454
R(5,6)	1.4114	A(2,5,17)	110.576	D(5,2,4,14)	57.6375
R(5,16)	1.1082	A(6,5,16)	110.573	D(5,2,4,15)	-62.7004
R(5,17)	1.1074	A(6,5,17)	109.2643	D(1,2,5,6)	-178.361
R(6,7)	1.5146	A(16,5,17)	107.6766	D(1,2,5,16)	60.4141
R(7,18)	0.943	A(5,6,7)	105.9077	D(1,2,5,17)	-58.5073
A(2,1,8)	111.6172	A(6,7,18)	94.7454	D(3,2,5,6)	-59.7009
A(2,1,9)	111.3767	D(8,1,2,3)	-59.7873	D(3,2,5,16)	179.0738
A(2,1,10)	110.9389	D(8,1,2,4)	179.5105	D(3,2,5,17)	60.1524
A(8,1,9)	107.6533	D(8,1,2,5)	58.6223	D(4,2,5,6)	62.1829
A(8,1,10)	107.4807	D(9,1,2,3)	179.854	D(4,2,5,16)	-59.0423
A(9,1,10)	107.576	D(9,1,2,4)	59.1517	D(4,2,5,17)	-177.964
A(1,2,3)	109.3926	D(9,1,2,5)	-61.7365	D(2,5,6,7)	-168.362
A(1,2,4)	108.9854	D(10,1,2,3)	60.0533	D(16,5,6,7)	-47.3729
A(1,2,5)	107.8243	D(10,1,2,4)	-60.6489	D(17,5,6,7)	70.9696
A(3,2,4)	110.3277	D(10,1,2,5)	178.4628	D(5,6,7,18)	-176.575
A(3,2,5)	109.0019	D(1,2,3,11)	34.816		

Table B.3 Geometry Parameters for Ts1

Ts1					
Definition	Value	Definition	Value	Definition	Value
R(1,2)	1.5252	A(2,3,12)	111.2599	D(1,2,3,13)	-59.144
R(1,9)	1.0985	A(2,3,13)	111.3595	D(1,2,3,14)	-179.2881
R(1,10)	1.098	A(2,3,14)	111.391	D(4,2,3,12)	179.7028
R(1,11)	1.0978	A(12,3,13)	107.4097	D(4,2,3,13)	59.9083
R(2,3)	1.5264	A(12,3,14)	107.6034	D(4,2,3,14)	-60.2359
R(2,4)	1.5565	A(13,3,14)	107.6154	D(5,2,3,12)	-60.8074
R(2,5)	1.5152	A(2,4,8)	111.5796	D(5,2,3,13)	179.3981
R(3,12)	1.0982	A(2,4,15)	112.4034	D(5,2,3,14)	59.2539
R(3,13)	1.0983	A(2,4,16)	110.695	D(1,2,4,8)	-164.7651
R(3,14)	1.0978	A(8,4,15)	101.5459	D(1,2,4,15)	81.9153
R(4,8)	1.4142	A(8,4,16)	111.5719	D(1,2,4,16)	-39.8706
R(4,15)	1.103	A(15,4,16)	108.7161	D(3,2,4,8)	75.7282
R(4,16)	1.1066	A(2,5,6)	107.689	D(3,2,4,15)	-37.5914
R(5,6)	1.3	A(2,5,17)	115.2656	D(3,2,4,16)	-159.3773
R(5,17)	1.092	A(2,5,18)	115.6699	D(5,2,4,8)	-44.7423
R(5,18)	1.0918	A(6,5,17)	102.9843	D(5,2,4,15)	-158.0619
R(7,8)	1.3962	A(6,5,18)	102.4049	D(5,2,4,16)	80.1522
A(2,1,9)	111.7881	A(17,5,18)	111.0787	D(1,2,5,6)	138.3241
A(2,1,10)	111.178	A(4,8,7)	111.2506	D(1,2,5,17)	24.0373
A(2,1,11)	111.0903	D(9,1,2,3)	-179.4345	D(1,2,5,18)	-107.8816
A(9,1,10)	107.5648	D(9,1,2,4)	60.8003	D(3,2,5,6)	-100.8221
A(9,1,11)	107.4957	D(9,1,2,5)	-58.094	D(3,2,5,17)	144.8911
A(10,1,11)	107.518	D(10,1,2,3)	60.3396	D(3,2,5,18)	12.9722
A(1,2,3)	109.351	D(10,1,2,4)	-59.4256	D(4,2,5,6)	19.3983
A(1,2,4)	108.6103	D(10,1,2,5)	-178.3199	D(4,2,5,17)	-94.8885
A(1,2,5)	110.3623	D(11,1,2,3)	-59.3569	D(4,2,5,18)	133.1926
A(3,2,4)	109.7651	D(11,1,2,4)	-179.1221	D(2,4,8,7)	66.6908
A(3,2,5)	110.1682	D(11,1,2,5)	61.9836	D(15,4,8,7)	-173.3676
A(4,2,5)	108.5584	D(1,2,3,12)	60.6505	D(16,4,8,7)	-57.7132

Table B.4 Geometry Parameters for Ts2

Ts2					
Definition	Value	Definition	Value	Definition	Value
R(1,2)	1.5272	A(3,4,10)	94.525	D(2,1,6,16)	173.4472
R(1,6)	1.4941	A(7,5,11)	110.8998	D(7,1,6,14)	-148.0363
R(1,7)	1.397	A(7,5,12)	126.4821	D(7,1,6,15)	92.5981
R(2,3)	1.3923	A(7,5,13)	85.5335	D(7,1,6,16)	-27.0412
R(2,8)	1.1075	A(11,5,12)	111.8627	D(2,1,7,5)	-94.0941
R(2,9)	1.1092	A(11,5,13)	109.9194	D(2,1,7,17)	163.051
R(3,4)	1.5293	A(12,5,13)	108.1169	D(2,1,7,18)	-20
R(4,10)	0.9423	A(1,6,14)	111.6181	D(6,1,7,5)	106.681
R(5,7)	1.9601	A(1,6,15)	110.3843	D(6,1,7,17)	3.826
R(5,11)	1.0891	A(1,6,16)	111.8644	D(6,1,7,18)	-179.2249
R(5,12)	1.0934	A(14,6,15)	107.3984	D(1,2,3,4)	-87.027
R(5,13)	1.0959	A(14,6,16)	107.8847	D(8,2,3,4)	39.6631
R(6,14)	1.0984	A(15,6,16)	107.4881	D(9,2,3,4)	155.2414
R(6,15)	1.099	A(1,7,5)	69.2807	D(2,3,4,10)	179.0748
R(6,16)	1.0981	A(1,7,17)	117.8184	D(11,5,7,1)	92.062
R(7,17)	1.0956	A(1,7,18)	117	D(11,5,7,17)	-154.8894
R(7,18)	1.09	A(5,7,17)	110.4353	D(11,5,7,18)	-28.7483
A(2,1,6)	115.6771	A(5,7,18)	86.1136	D(12,5,7,1)	-49.0279
A(2,1,7)	117.208	A(17,7,18)	125.1034	D(12,5,7,17)	64.0206
A(6,1,7)	124.0267	D(6,1,2,3)	66.5257	D(12,5,7,18)	-169.8383
A(1,2,3)	113.2793	D(6,1,2,8)	-60.7939	D(13,5,7,1)	-158.3062
A(1,2,8)	111.0186	D(6,1,2,9)	177.5797	D(13,5,7,17)	-45.2576
A(1,2,9)	110.7837	D(7,1,2,3)	-94.4373	D(13,5,7,18)	80.8835
A(3,2,8)	112.216	D(7,1,2,8)	138.243		
A(3,2,9)	99.6883	D(7,1,2,9)	16.6166		
A(8,2,9)	109.2909	D(2,1,6,14)	52.4521		
A(2,3,4)	108.5782	D(2,1,6,15)	-66.9135		

Table B.5 Geometry Parameters for Ts3

Ts3					
Definition	Value	Definition	Value	Definition	Value
R(1,2)	2.0964	A(8,2,9)	116.7682	D(2,1,5,12)	-57.4563
R(1,5)	1.4995	A(2,3,4)	108.614	D(2,1,5,13)	-176.734
R(1,6)	1.4978	A(3,4,10)	94.8215	D(6,1,5,11)	169.9321
R(1,7)	1.3643	A(1,5,11)	112.0185	D(6,1,5,12)	48.9857
R(2,3)	1.3453	A(1,5,12)	111.87	D(6,1,5,13)	-70.2915
R(2,8)	1.0911	A(1,5,13)	110.1766	D(7,1,5,11)	-35.4462
R(2,9)	1.0912	A(11,5,12)	107.6239	D(7,1,5,12)	-156.393
R(3,4)	1.5347	A(11,5,13)	107.6278	D(7,1,5,13)	84.3302
R(4,10)	0.9421	A(12,5,13)	107.308	D(2,1,6,14)	52.3132
R(5,11)	1.0981	A(1,6,14)	111.6996	D(2,1,6,15)	-68.576
R(5,12)	1.0986	A(1,6,15)	112.0674	D(2,1,6,16)	171.595
R(5,13)	1.0985	A(1,6,16)	110.1753	D(5,1,6,14)	-51.9792
R(6,14)	1.0984	A(14,6,15)	107.6466	D(5,1,6,15)	-172.868
R(6,15)	1.0978	A(14,6,16)	107.4	D(5,1,6,16)	67.3026
R(6,16)	1.0986	A(15,6,16)	107.6447	D(7,1,6,14)	153.5414
R(7,17)	1.085	A(1,7,17)	122.4654	D(7,1,6,15)	32.6522
R(7,18)	1.0851	A(1,7,18)	122.4201	D(7,1,6,16)	-87.1768
A(2,1,5)	97.8713	A(17,7,18)	115.1129	D(2,1,7,17)	91.7996
A(2,1,6)	101.358	D(5,1,2,3)	167.9843	D(2,1,7,18)	-87.7177
A(2,1,7)	93.7672	D(5,1,2,8)	56.7777	D(5,1,7,17)	-166.918
A(5,1,6)	114.8327	D(5,1,2,9)	-63.239	D(5,1,7,18)	13.5651
A(5,1,7)	119.7305	D(6,1,2,3)	50.5839	D(6,1,7,17)	-13.6785
A(6,1,7)	120.2486	D(6,1,2,8)	-60.6226	D(6,1,7,18)	166.8041
A(1,2,3)	112.0807	D(6,1,2,9)	179.3607	D(1,2,3,4)	97.1992
A(1,2,8)	98.7402	D(7,1,2,3)	-71.2969	D(8,2,3,4)	-156.172
A(1,2,9)	102.3768	D(7,1,2,8)	177.4966	D(9,2,3,4)	-22.1727
A(3,2,8)	105.9135	D(7,1,2,9)	57.4799	D(2,3,4,10)	-165.136
A(3,2,9)	119.0972	D(2,1,5,11)	63.4901		

Table B.6 Geometry Parameters for Ts4

Ts4					
Definition	Value	Definition	Value	Definition	Value
R(1,2)	1.518	A(2,3,6)	96.7468	D(4,2,3,6)	-120.372
R(1,7)	1.0978	A(2,3,10)	114.6498	D(4,2,3,10)	123.5178
R(1,8)	1.0978	A(2,3,11)	113.9366	D(4,2,3,11)	-2.1568
R(1,9)	1.0982	A(6,3,10)	110.3787	D(5,2,3,6)	-3.044
R(2,3)	1.5515	A(6,3,11)	112.4246	D(5,2,3,10)	-119.154
R(2,4)	1.5179	A(10,3,11)	108.3751	D(5,2,3,11)	115.1713
R(2,5)	1.5113	A(2,4,12)	111.1125	D(1,2,4,12)	-59.3398
R(3,6)	1.4242	A(2,4,13)	111.6485	D(1,2,4,13)	-179.45
R(3,10)	1.1031	A(2,4,14)	111.0281	D(1,2,4,14)	60.4796
R(3,11)	1.1041	A(12,4,13)	107.5836	D(3,2,4,12)	174.1972
R(4,12)	1.0978	A(12,4,14)	107.6828	D(3,2,4,13)	54.0872
R(4,13)	1.0982	A(13,4,14)	107.5978	D(3,2,4,14)	-65.9834
R(4,14)	1.0978	A(2,5,15)	119.4066	D(5,2,4,12)	67.7096
R(5,15)	1.0885	A(2,5,16)	119.727	D(5,2,4,13)	-52.4005
R(5,16)	1.0892	A(15,5,16)	114.6988	D(5,2,4,14)	-172.471
R(6,17)	1.6307	A(3,6,17)	107.7341	D(1,2,5,15)	138.8688
R(17,18)	0.9389	A(6,17,18)	91.9868	D(1,2,5,16)	-12.0783
A(2,1,7)	111.1151	D(7,1,2,3)	-173.996	D(3,2,5,15)	-104.09
A(2,1,8)	111.0213	D(7,1,2,4)	59.508	D(3,2,5,16)	104.9625
A(2,1,9)	111.6921	D(7,1,2,5)	-67.5583	D(4,2,5,15)	13.0276
A(7,1,8)	107.6593	D(8,1,2,3)	66.2172	D(4,2,5,16)	-137.92
A(7,1,9)	107.5845	D(8,1,2,4)	-60.2789	D(2,3,6,17)	156.555
A(8,1,9)	107.5783	D(8,1,2,5)	172.6547	D(10,3,6,17)	-83.9751
A(1,2,3)	112.4068	D(9,1,2,3)	-53.8533	D(11,3,6,17)	37.1621
A(1,2,4)	110.4386	D(9,1,2,4)	179.6505	D(3,6,17,18)	173.7978
A(1,2,5)	112.6956	D(9,1,2,5)	52.5842		
A(3,2,4)	112.4663	D(1,2,3,6)	114.2306		
A(3,2,5)	95.4097	D(1,2,3,10)	-1.8795		
A(4,2,5)	112.7262	D(1,2,3,11)	-127.554		

Table B.7 Geometry Parameters for Ts5

Ts5					
Name	Definition	Value	Name	Definition	Value
R1	r21	1.5416	D8	a1012	110.1894
R2	r32	1.5393	D9	a1132	111.3657
R3	r42	1.5402	D10	a1232	110.0959
R4	r52	1.5392	D11	a1332	103.3571
R5	r65	1.27	D12	a1442	110.4496
R6	r76	1.3108	D13	a1542	111.281
R7	r81	1.0958	D14	a1642	111.1882
R8	r91	1.0958	D15	a1752	110.8246
A1	r101	1.0948	D16	a1852	112.1346
A2	r113	1.0951	D17	d4213	238.7672
A3	r123	1.0953	D18	d5213	119.7585
A4	r133	1.2242	D19	d6521	176.8157
A5	r144	1.095	D20	d7652	81.7331
A6	r154	1.096	D21	d8123	300.6981
A7	r164	1.0936	D22	d9123	179.7421
A8	r175	1.0953	D23	d10123	60.1983
A9	r185	1.0926	D24	d11321	58.641
D1	a321	109.7826	D25	d12321	298.9215
D2	a421	109.856	D26	d13321	167.4603
D3	a521	106.7553	D27	d14421	61.6665
D4	a652	112.298	D28	d15421	302.0225
D5	a765	106.3276	D29	d16421	181.5865
D6	a812	111.5525	D30	d17521	60.7971
D7	a912	111.5784	D31	d18521	297.2082

Table B.8 Vibration Frequencies (cm^{-1})

Species	V1^b	v2	v3	v4	v5	v6	v7	v8	v9	v10	v11	v12
	V13	v14	v15	v16	v17	v18	v19	v20	v21	v22	v23	v24
	v25	v26	v27	v28	v29	v30	v31	v32	v33	v34	v35	v36
	v37	v38	v39	v40	v41	v42	v43	v44	v45	v46	v47	v48
C_3CCOO•	49.82	125.13	178.45	220.05	265.58	271.1	325.48	328.36	358.19	412.41	452.82	519.07
	766.36	912.68	933.42	950.7	952.99	957	969.37	1065.65	1078.66	1201.24	1206.92	1250.01
	1292.31	1305.56	1384.82	1413.12	1414.7	1446.02	1494.56	1495.17	1503.39	1504.84	1520.79	1522.37
	1535.89	3036.1	3040.49	3045.55	3058.96	3105.19	3108.43	3109.87	3115.9	3117.98	3127.42	3131.33
C_3•CCOOH	86.02	101.1	118.12	177.8	210.18	236.26	265.62	312.43	325.6	346.06	412.86	441.16
	472.87	566.76	779.18	916.12	921.29	941.22	955	962.53	1007.02	1046.88	1087.17	1208.59
	1224.40	1249.52	1305.73	1364.5	1383.4	1408.42	1427.59	1477.29	1501.02	1501.93	1515.76	1523.15
	1533.25	3001.46	3038.82	3046.39	3052.92	3108.79	3113.84	3122.1	3137.19	3151.93	3260.49	3748.61
Ts1	111.25	230.78	248.18	275.55	306.21	324	391.09	430.54	455.26	485.42	547.6	646.99
	761.84	886.89	914.94	943.33	947.19	971.96	1003.59	1030.97	1050.94	1073.62	1136.63	1210.05
	1233.48	1251.31	1316.99	1364.74	1409.17	1428.12	1468.35	1481.05	1500.93	1507.06	1516.8	1523.98
	1587.85	3034.62	3038.85	3045.85	3100.45	3104.7	3107.93	3113.45	3121.07	3134.33	3191.56	
Ts2	55.29	95.2	130.94	190.28	251.36	265.36	323.17	357.46	376.31	397.14	497.76	596.37
	628.72	689.28	803.02	871.58	946.11	954.54	960.49	975.81	1004.5	1045.28	1103.12	1244.09
	1297.37	1325.18	1344.22	1373.22	1390.9	1420.03	1432.2	1464.46	1477.6	1500.53	1506.45	1525.59
	2841.11	2998.96	3006.93	3016.49	3066.01	3071.26	3099.6	3111.24	3161.45	3269.9	3698.43	
Ts3	35.2	93.45	144.98	157.03	191.94	204.85	225.44	260.02	371.19	383.06	418.08	452.48
	566.35	599.73	779.42	796.02	812	941.52	957.47	975.99	1028.98	1066.77	1080.49	1105.6
	1207.09	1291.86	1392.94	1406.4	1418.21	1434.8	1452.32	1493.35	1500.73	1506.34	1514.48	1569.99
	3028.78	3033.05	3089.2	3091.13	3095.79	3119.32	3141.09	3153.01	3222.49	3245.1	3769.81	
Ts4	72.42	137.26	154.53	212.94	245.9	285.63	314.09	327.81	398.35	413.75	427.44	543.5
	570.59	781.29	826.49	913.17	930.38	959.69	971.06	1002.89	1013.59	1061.76	1100.58	1187.72
	1232.61	1248.88	1292.16	1350.4	1411.16	1427.48	1482.1	1501.5	1502.59	1515.46	1524.9	1535.88
	3018.99	3035.95	3042.21	3089.61	3107.06	3112.57	3114.11	3124.12	3153.81	3260.5	3788.59	
Ts5	65.27	96.76	146.85	184.69	211.62	268.74	289.67	296.57	388.69	396.53	416.37	468.36
	550.69	620.66	821.49	836.49	850.67	950.43	957.68	962.28	1039.67	1066.35	1112.67	1168.96
	1213.57	1224.55	1304.68	1309.67	1319.66	1332.67	1335.62	1512.37	1521.44	1532.46	1542.22	1556.31
	3021.37	3033.51	3048.69	3066.58	3104.51	3118.64	3124.29	3132.24	3164.27	3251.49	3784.63	

Table B.9 Moments of Inertia

Species	Moments of Inertia		
	Ia^b	Ib	Ic
C_3CCOO•	422.39	1161.9	1171.9
C_3•CCOOH	416.03	1185.8	1204.7
Ts1	456.06	932.85	974.63
Ts2	459.07	990.48	1100.5
Ts3	485.44	1135.1	1195.9
Ts4	395.25	1168.4	1190.1
Ts5	401.68	1147.8	1192.4

[a] Optimized at the B3lyp/6-31G(d,p) level of theory. [b] Units in amu-Bohr^2.

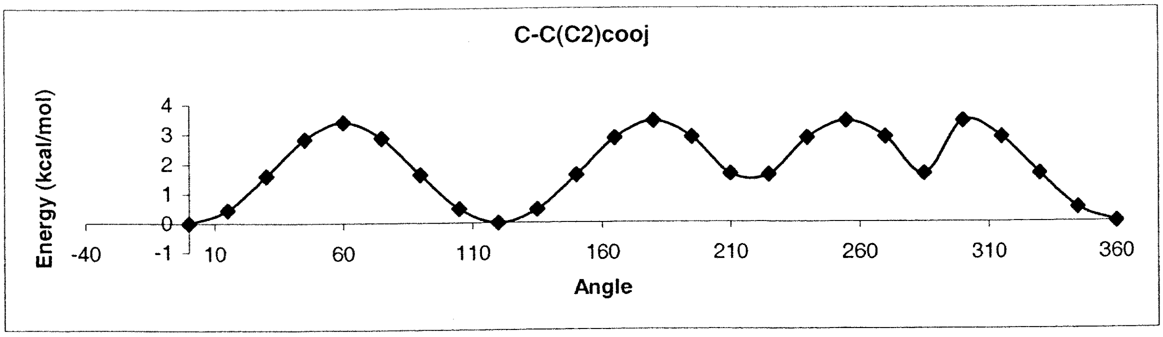


Figure B.1 Internal Rotation Barriers about C(C_3H_9)CCOO·

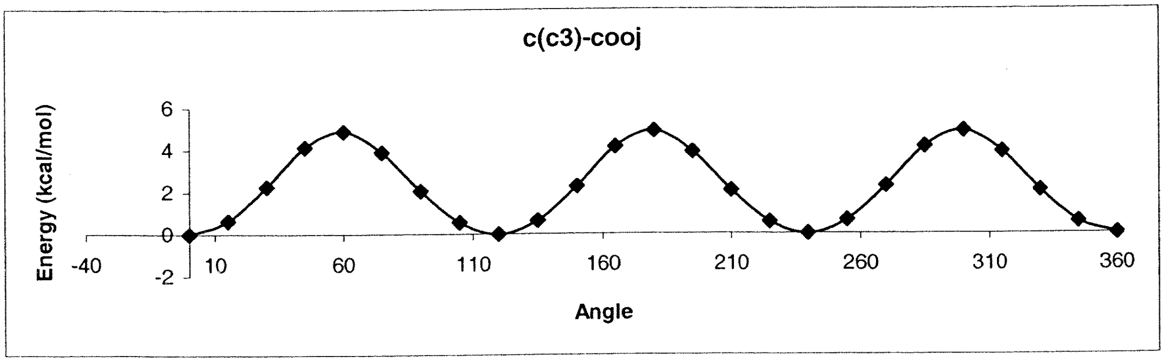


Figure B.2 Internal Rotation Barriers about C(C_3H_9)CCOO·

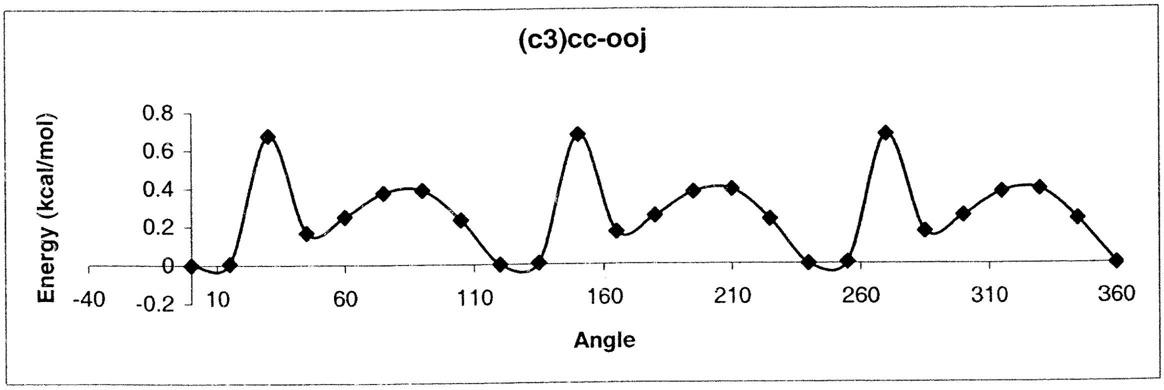


Figure B.3 Internal Rotation Barriers about C(C_3H_9)CCOO·

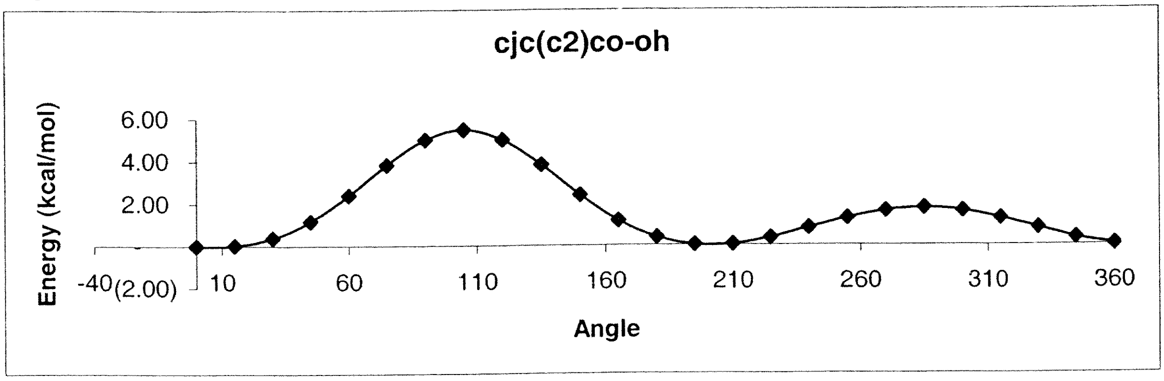


Figure B.4 Internal Rotation Barriers about C·H_2(C_2H_6)CCOOH

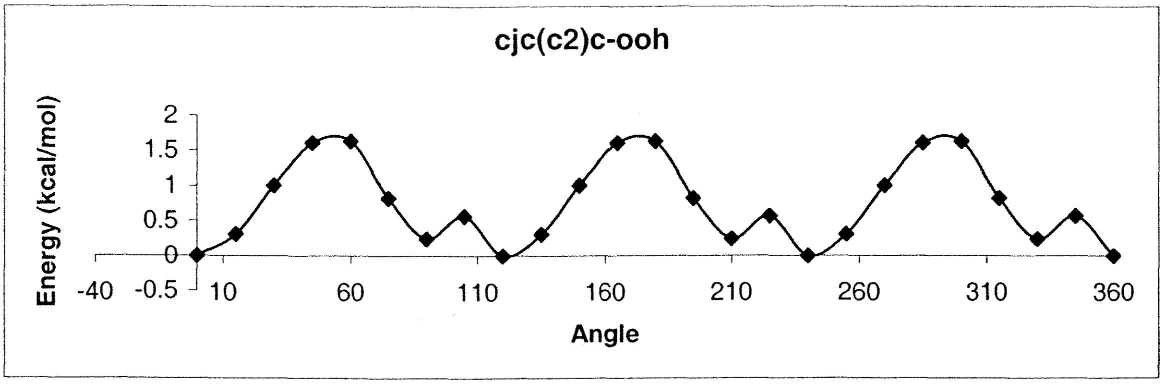


Figure B.5 Internal Rotation Barriers about C·$H_2(C_2H_6)$CCOOH

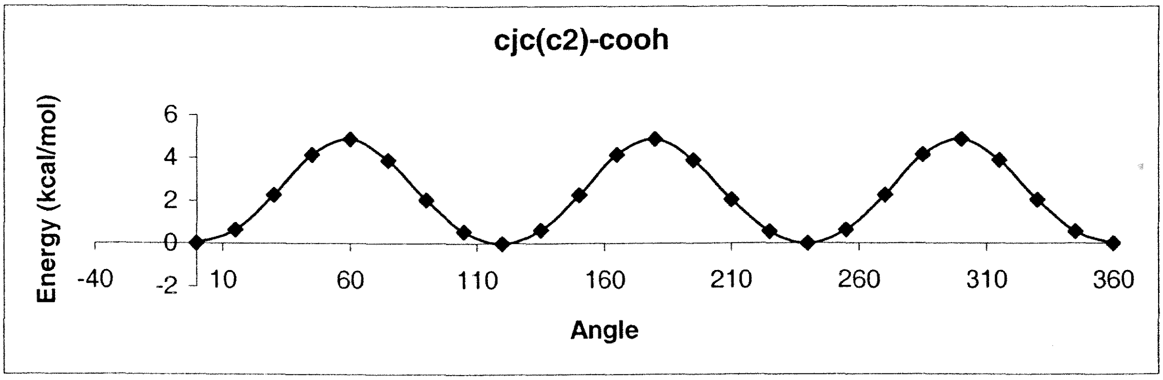


Figure B.6 Internal Rotation Barriers about C·$H_2(C_2H_6)$CCOOH

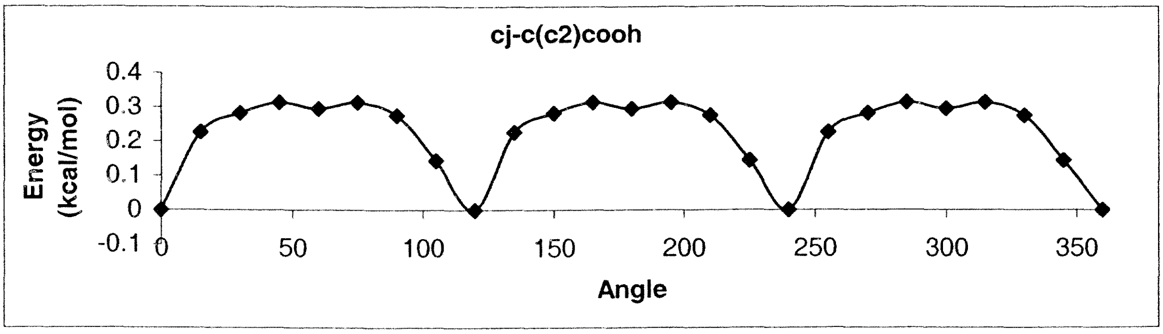


Figure B.7 Internal Rotation Barriers about C·$H_2(C_2H_6)$CCOOH

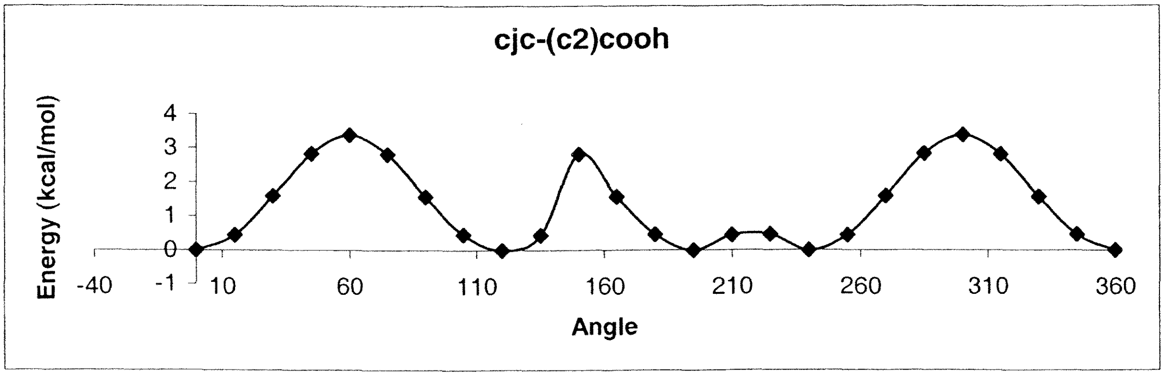


Figure B.8 Internal Rotation Barriers about C·$H_2(C_2H_6)$CCOOH

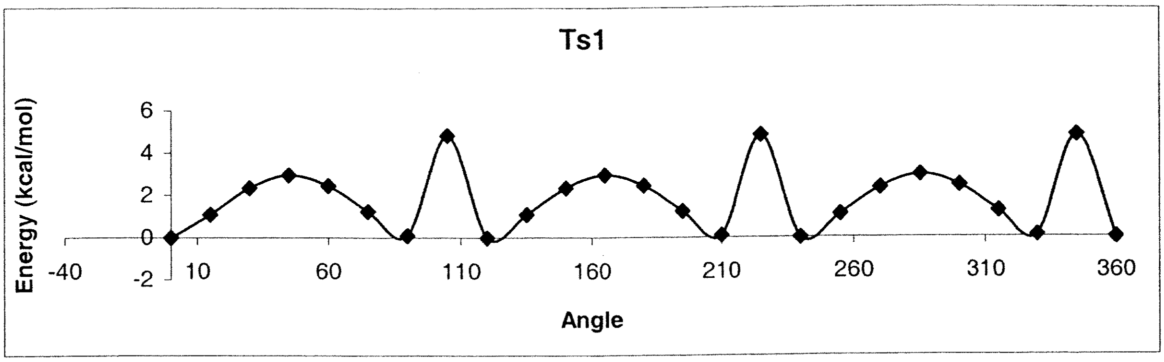


Figure B.9 Internal Rotation Barriers about TS1

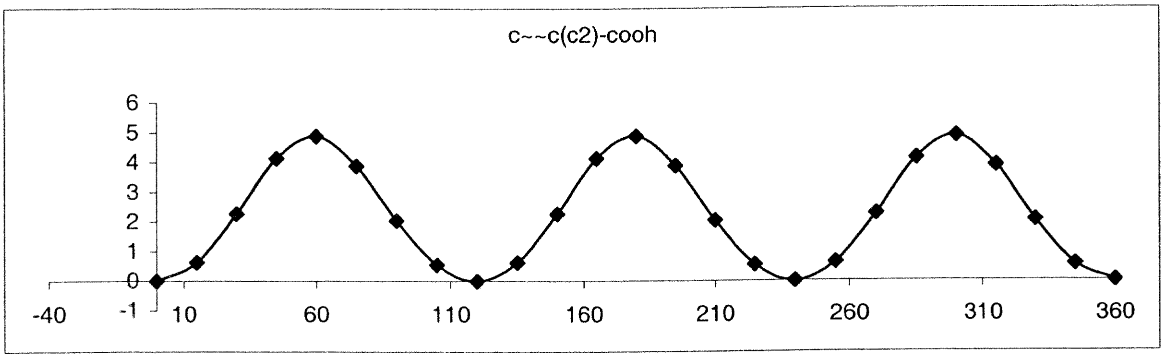


Figure B.10 Internal Rotation Barriers about Ts2

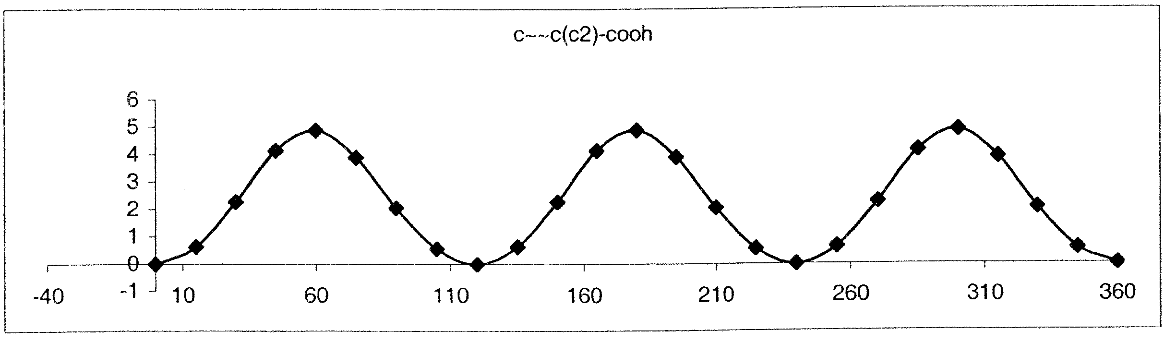


Figure B.11 Internal Rotation Barriers about Ts2

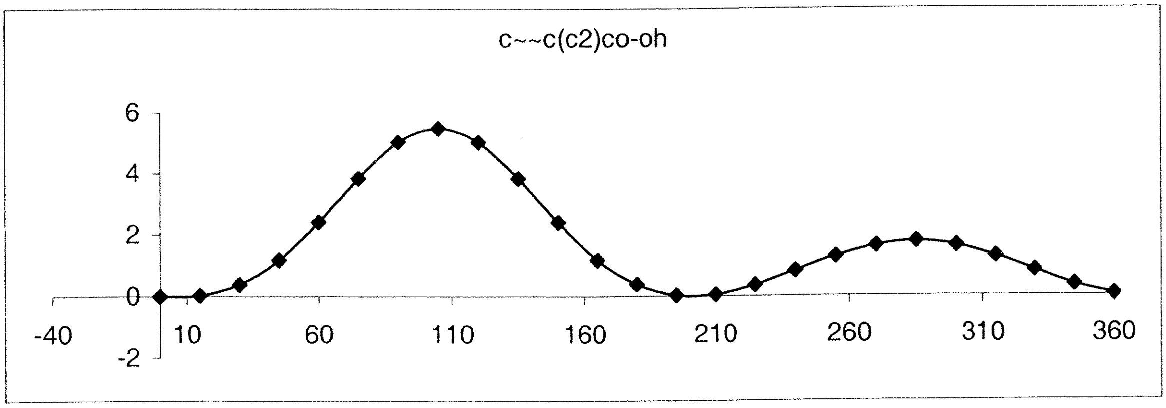


Figure B.12 Internal Rotation Barriers about TS2

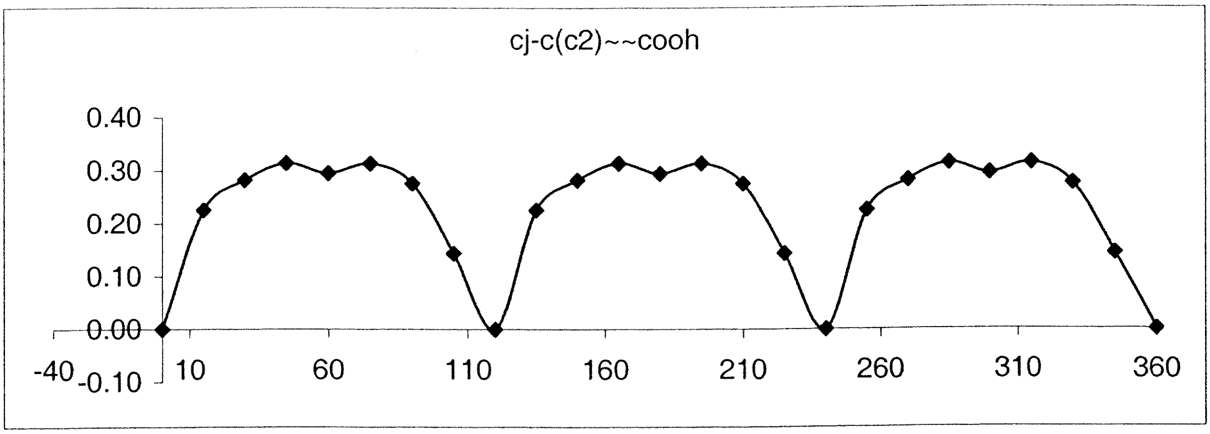


Figure B.13 Internal Rotation Barriers about Ts3

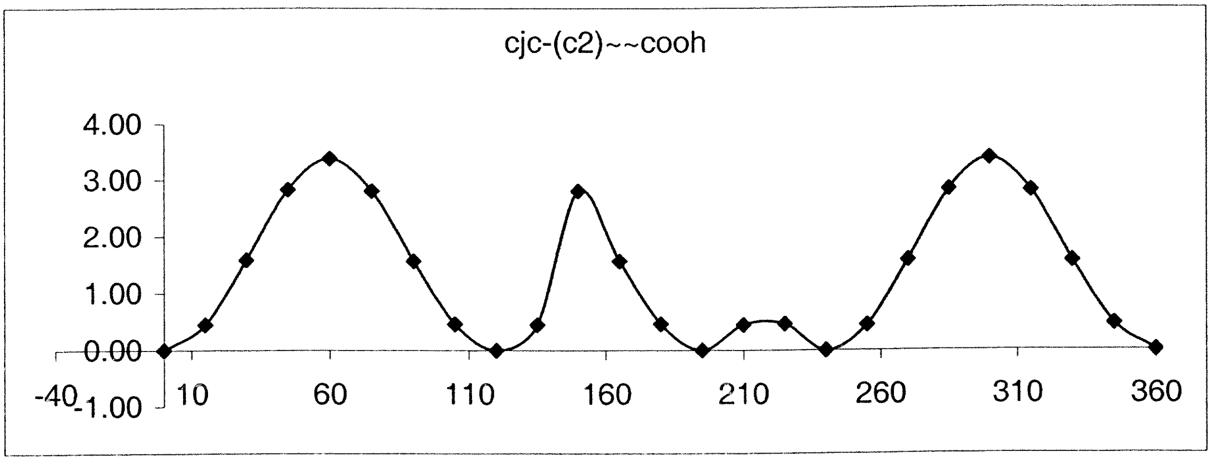


Figure B.14 Internal Rotation Barriers about Ts3

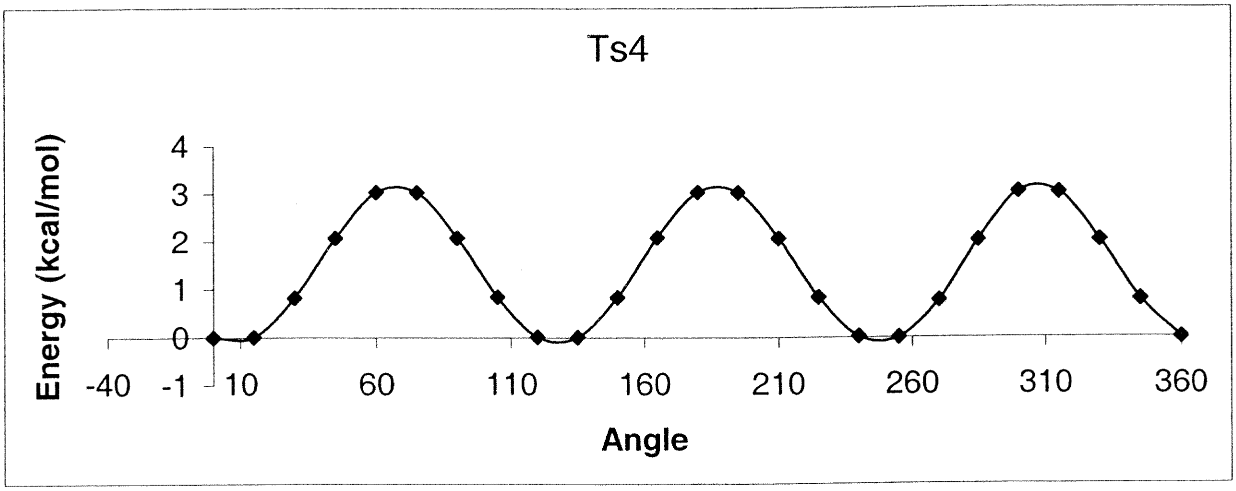


Figure B.15 Internal Rotation Barriers about Ts4

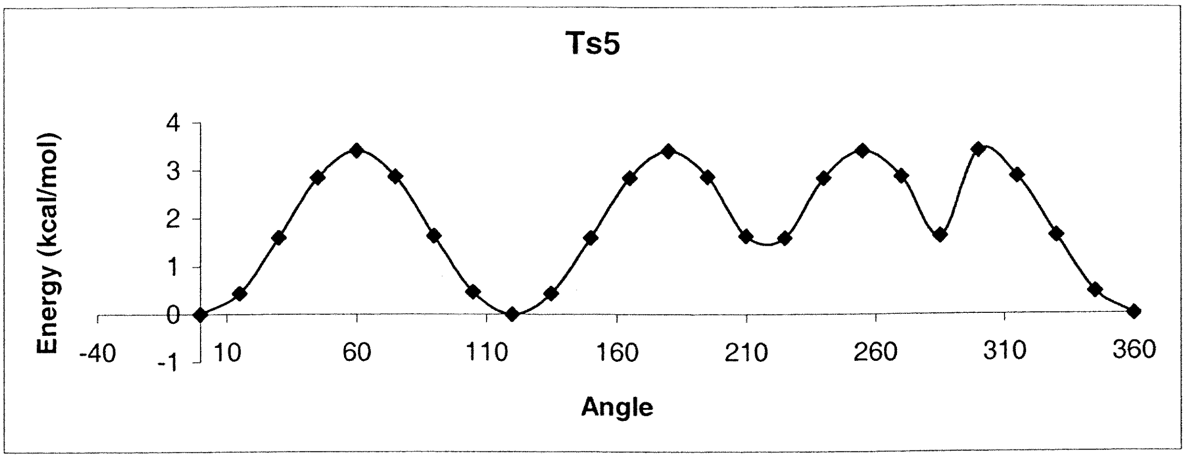


Figure B.16 Internal Rotation Barriers about Ts5

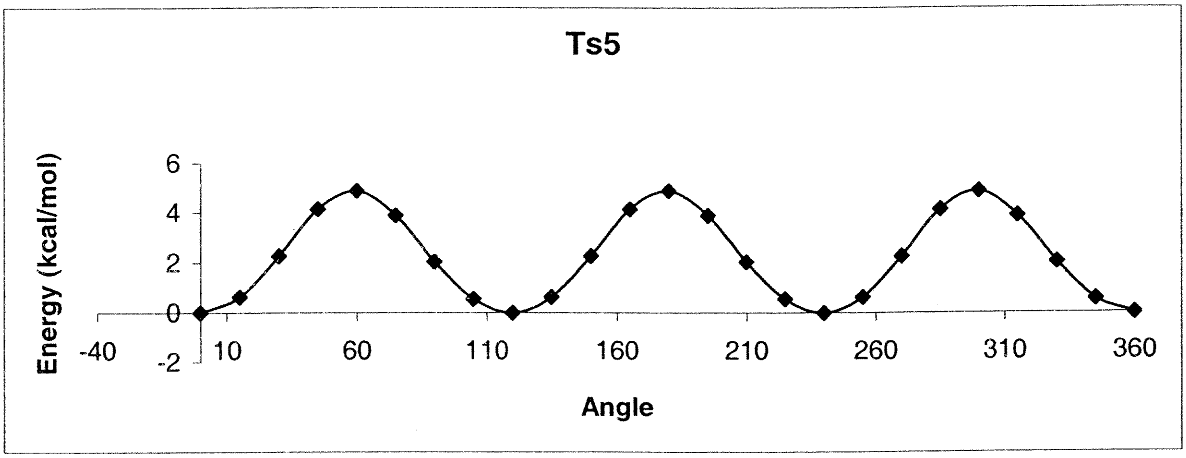


Figure B.17 Internal Rotation Barriers about Ts5

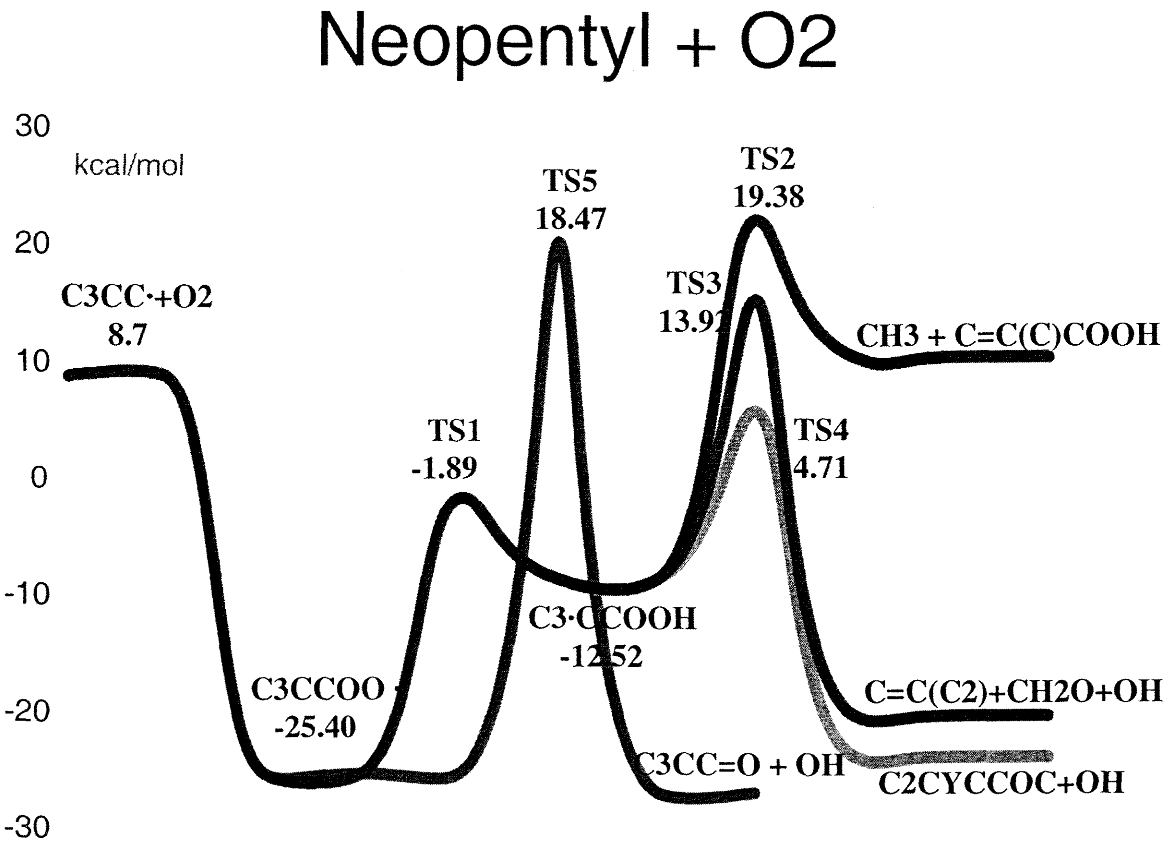


Figure B.18 Overview Schematic of Neopentyl + O_2 Paths

Table B.10 Thermodynamic Properties for Species

SPECIES	HF(298)	S(298)	C_P : 300	400	500	600	800	1000	1500
OH	9.50	43.80	6.79	6.89	6.93	7.00	7.14	7.28	7.43
H_2	0.00	31.21	6.90	6.95	6.99	7.02	7.10	7.21	7.72
O_2	0.00	49.01	7.02	7.23	7.44	7.65	8.04	8.35	8.73
$C_3CCOO\cdot$	-25.40	69.28	35.81	43.75	50.45	56.01	64.68	71.18	81.50
$C_3\cdot CCOOH$	-12.52	75.83	37.92	44.78	50.99	56.26	64.53	70.72	80.66
TS1	-1.89	74.33	29.46	38.23	46.12	52.78	63.04	70.45	81.62
TS2	19.38	73.47	31.61	39.38	46.24	51.97	60.80	67.31	77.57
TS3	13.92	73.78	31.82	38.92	45.30	50.75	59.41	65.98	76.60
TS4	4.71	77.78	33.40	41.89	49.09	55.00	64.09	70.83	81.57
TS5	18.47	78.31	30.33	39.84	47.39	53.58	65.31	70.21	80.61

Table B.11-a Input data for Smcps

```
NAME (name of molecule)
c3ccooj
COMMENTS:
C3CCOOJ
TEMPERATURE
8     (Number of temperature to be read in)
298 300 400 500 600 800 1000 1500 (Values of temperature)
ROTOR
5    number of internal rotors
MOLECULAR WT
103.07590
OPTICAL ISOMER
1
MULTIPLICITY
2       multiplicity of molecular specie of interest
HF298
-154.3868089
STOICHIOMETRY (in form of "atom x" "number of atom x")
H 11  C 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).
rem RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
0.9806               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3    choice of moment of inertia units
422.38889  1161.93941  1171.91495
SYMMETRY
81

NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
48
49.8209               125.1330              178.4544
220.0462              265.5846              271.0994
325.4753              328.3601              358.1882
412.4104              452.8222              519.0654
766.3601              912.6806              933.4184
950.7007              952.9931              957.0015
969.3680             1065.6457             1078.6570
1201.2395            1206.9247             1250.0117
1292.3132            1305.5568             1384.8206
1413.1220            1414.7021             1446.0204
1494.5555            1495.1689             1503.3857
1504.8374            1520.7938             1522.3663
1535.8875            3036.1017             3040.4918
3045.5465            3058.9576             3105.1917
3108.4277            3109.8729             3115.8985
3117.9773            3127.4167             3131.3253
```

Table B.11-b Input data for Smcps

```
NAME (name of molecule)
c3.ccooh
COMMENTS:
This molecule is called.
TEMPERATURE
8    (Number of temperature to be read in)
298  300   400   500   600   800   1000   1500 (Values of temperature)
ROTOR
7   number of internal rotors
MOLECULAR WT
103.07590
OPTICAL ISOMER
2
MULTIPLICITY
2       multiplicity of molecular specie of interest
HF298
-154.3868089
STOICHIOMETRY (in form of "atom x" "number of atom x")
H 11  C 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).
rem RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
0.9806               (integer input)
rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)
MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3    choice of moment of inertia units
416.03473  1185.75411   1204.66728
SYMMETRY
81
NON-LINEAR
FREQ (The format for the frequencies is not important.  Units are cm-1)
48
86.0243                  101.1047                 118.1179
177.8033                 210.1753                 236.2638
265.6209                 312.4296                 325.5993
346.0596                 412.8572                 441.1586
472.8704                 566.7563                 779.1753
916.1155                 921.2857                 941.2198
954.9978                 962.5320                1007.0180
1046.8808                1087.1673                1208.5884
1224.4012                1249.5228                1305.7307
1364.4999                1383.3960                1408.4220
1427.5899                1477.2862                1501.0194
1501.9348                1515.7573                1523.1541
1533.2507                3001.4597                3038.8220
3113.8387                3122.1034                3137.1871
3151.9311                3260.4894                3748.6122
```

Table B.11-c Input data for Smcps

```
NAME (name of molecule)
Ts1
COMMENTS:
This molecule is called.
TEMPERATURE
8    (Number of temperature to be read in)
298  300   400   500   600   800   1000   1500 (Values of temperature)
ROTOR
3    number of internal rotors
MOLECULAR WT
103.07590
OPTICAL ISOMER
1
MULTIPLICITY
2       multiplicity of molecular specie of interest
HF298
-154.3868089
STOICHIOMETRY (in form of "atom x" "number of atom x")
H 11  C 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).
rem RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
0.9806               (integer input)
rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)
MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3    choice of moment of inertia units
456.05610  932.84675  974.62749
SYMMETRY
9
NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
47
111.2506              230.7788
248.1763              275.5487               306.2078
323.9983              391.0907               430.5384
455.2599              485.4170               547.5953
646.9945              761.8420               886.8926
914.9444              943.3318               947.1861
971.9617             1003.5893              1030.9734
1050.9444             1073.6225              1136.6281
1210.0476             1233.4790              1251.3067
1316.9914             1364.7353              1409.1683
1428.1187             1468.3481              1481.0467
1500.9259             1507.0581              1516.7986
1523.9830             1587.8489              3034.6181
3038.8492             3045.8500              3100.4494
3104.6976             3107.9277              3113.4516
3121.0699             3134.3323              3191.5550
```

Table B.11-d Input data for Smcps

```
NAME (name of molecule)
Ts2
COMMENTS:
This molecule is called.
TEMPERATURE
8    (Number of temperature to be read in)
298  300   400   500   600   800   1000   1500(Values of temperature)
ROTOR
6    number of internal rotors
MOLECULAR WT
103.07590
OPTICAL ISOMER
2
MULTIPLICITY
2       multiplicity of molecular specie of interest
HF298
-154.3868089
STOICHIOMETRY (in form of "atom x" "number of atom x")
H 11  C 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).
rem RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
0.9806               (integer input)
rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)
MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3    choice of moment of inertia units
459.07241  990.47932  1100.46730
SYMMETRY
9
NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
47
55.2931                  95.2038
130.9395                 190.2795                 251.3557
265.3571                 323.1696                 357.4585
376.3084                 397.1366                 497.7621
596.3735                 628.7200                 689.2799
803.0216                 871.5775                 946.1050
954.5352                 960.4877                 975.8098
1004.4958                1045.2781                1103.1177
1244.0897                1297.3690                1325.1761
1344.2170                1373.2246                1390.8998
1420.0292                1432.1980                1464.4600
1477.6010                1500.5318                1506.4482
1525.5860                2841.1139                2998.9589
3006.9298                3016.4903                3066.0058
3071.2596                3099.5969                3111.2371
3161.4520                3269.8993                3698.4262
```

Table B.11-e Input data for Smcps

```
NAME (name of molecule)
Ts3
COMMENTS:
This molecule is called.
TEMPERATURE
8    (Number of temperature to be read in)
298  300   400   500   600   800   1000  1500(Values of temperature)
ROTOR
6    number of internal rotors
MOLECULAR WT
103.07590
OPTICAL ISOMER
2
MULTIPLICITY
2       multiplicity of molecular specie of interest
HF298
-154.3868089
STOICHIOMETRY (in form of "atom x" "number of atom x")
H 11  C 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).
rem RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
0.9806               (integer input)
rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)
MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3    choice of moment of inertia units
485.44325  1135.07083  1195.91466
SYMMETRY
27
NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
47
35.2025                93.4525
144.9816               157.0284               191.9426
204.8528               225.4426               260.0171
371.1919               383.0602               418.0847
452.4831               566.3517               599.7302
779.4235               796.0176               811.9951
941.5238               957.4737               975.9934
1028.9771              1066.7748              1080.4896
1105.5984              1207.0887              1291.8578
1392.9445              1406.3950              1418.2061
1434.8024              1452.3227              1493.3458
1500.7292              1506.3372              1514.4760
1569.9920              3028.7823              3033.0480
3089.2038              3091.1288              3095.7949
3119.3175              3141.0947              3153.0119
3222.4881              3245.0966              3769.8094
```

Table B.11-f Input data for Smcps

```
NAME (name of molecule)
Ts4
COMMENTS:
This molecule is called.
TEMPERATURE
8    (Number of temperature to be read in)
298  300   400   500   600   800   1000   1500 (Values of temperature)
ROTOR
3    number of internal rotors
MOLECULAR WT
103.07590
OPTICAL ISOMER
1
MULTIPLICITY
2       multiplicity of molecular specie of interest
HF298
-154.3868089
STOICHIOMETRY (in form of "atom x" "number of atom x")
H 11  C 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).
rem RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
0.9806               (integer input)
rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)
MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3    choice of moment of inertia units
395.25070  1168.44288  1190.10550
SYMMETRY
9
NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
47
72.4172              137.2573
154.5344              212.9440               245.9008
285.6304              314.0931               327.8093
398.3520              413.7490               427.4413
543.5045              570.5912               781.2909
826.4864              913.1711               930.3774
959.6856              971.0578               1002.8922
1013.5922             1061.7580              1100.5835
1187.7181             1232.6138              1248.8780
1292.1610             1350.4049              1411.1626
1427.4849             1482.0981              1501.4979
1502.5898             1515.4615              1524.9020
1535.8829             3018.9918              3035.9549
3042.2058             3089.6057              3107.0648
3112.5715             3114.1079              3124.1223
3153.8120             3260.4980              3788.5923
```

Table B.12-a A Factor Calculation

```
THERMODYNAMIC ANALYSIS for REACTION
 Rx         C3.CCOOH   = TS1
 Hf {Kcal/mol}  -12.520    -1.890
 S {cal/mol K}  100.410    87.390

 dHr {kcal/mol}   (298K) =      10.63   dHr avg (298., 1500. K) =      11.42
 dU (dE) {kcal/mol} (") =      10.63   dUr avg (298., 1500. K) =      11.42
 dSr {cal/mol K}  ( " ) =     -13.02   dSr avg (298., 1500. K) =     -13.09
 dGr  {kcal/mol}  ( " ) =      14.51   dGr avg (298., 1500. K) =      23.19
    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)       Kc      dG(Kcal/mol)
    300.00   1.062E+01    1.062E+01  -1.306E+01    2.568E-11   1.454E+01
    400.00   1.015E+01    1.015E+01  -1.442E+01    2.005E-09   1.592E+01
    500.00   9.855E+00    9.855E+00  -1.509E+01    2.482E-08   1.740E+01
    600.00   9.714E+00    9.714E+00  -1.535E+01    1.280E-07   1.892E+01
    800.00   9.805E+00    9.805E+00  -1.523E+01    9.824E-07   2.199E+01
   1000.00   1.026E+01    1.026E+01  -1.473E+01    3.453E-06   2.499E+01
   1200.00   1.095E+01    1.095E+01  -1.410E+01    8.381E-06   2.787E+01
   1500.00   1.221E+01    1.221E+01  -1.316E+01    2.203E-05   3.196E+01
   2000.00   1.446E+01    1.446E+01  -1.187E+01    6.678E-05   3.821E+01
The equation to the 2 parameter model of A(T)
 for A(T) = Aprime * T^n
    Aprime = 1.2290E+06        n =   1.39609
```

```
 THERMODYNAMIC ANALYSIS for REACTION
 Rx         C3.CCOOH   = TS2
 Hf {Kcal/mol}  -12.520    19.380
 S {cal/mol K}  100.410    101.870

 dHr {kcal/mol}   (298K) =      31.90   dHr avg (298., 1500. K) =      30.42
 dU (dE) {kcal/mol} (") =      31.90   dUr avg (298., 1500. K) =      30.42
 dSr {cal/mol K}  ( " ) =       1.46   dSr avg (298., 1500. K) =       -.55
 dGr  {kcal/mol}  ( " ) =      31.46   dGr avg (298., 1500. K) =      30.91
The equation to the 2 parameter model of A(T)
 for A(T) = Aprime * T^n
    Aprime = 4.7212E+13        n =  -.23271
```

```
 THERMODYNAMIC ANALYSIS for REACTION
 Rx         C3CCOOJ    = TS5
 Hf {Kcal/mol}  -25.400    18.470
 S {cal/mol K}  95.050     88.870

 dHr {kcal/mol}   (298K) =      43.87   dHr avg (298., 1500. K) =      43.57
 dU (dE) {kcal/mol} (") =      43.87   dUr avg (298., 1500. K) =      43.57
 dSr {cal/mol K}  ( " ) =      -6.18   dSr avg (298., 1500. K) =      -6.21
 dGr  {kcal/mol}  ( " ) =      45.71   dGr avg (298., 1500. K) =      49.16
         Kc     ( " ) =    3.083E-34   Kc avg (298., 1500. K ) =  1.121E-12
 Fit Af/Ar      : A = 3.673E-04 n =   .92 alpha = 1.286E-03 avg error   2.82 %
 Fit Af/Ar w/ddU: A = 2.489E-05 n =  1.45 alpha = 2.211E-03 avg error   7.18 %

  The model fitted is for uni-molecular reaction.

 The equation to the 2 parameter model of A(T)
 for A(T) = Aprime * T^n
    Aprime = 3.7077E+09        n =   .81157
```

Table B. 12-b A Factor Calculation

```
THERMODYNAMIC ANALYSIS for REACTION
Rx        C3.CCOOH   = TS1
Hf {Kcal/mol}  -12.520    -1.890
S {cal/mol K}  100.410    87.390

dHr {kcal/mol}   (298K) =      10.63    dHr avg (298., 1500. K) =      11.42
dU (dE) {kcal/mol} (") =      10.63    dUr avg (298., 1500. K) =      11.42
dSr {cal/mol K}  ( " ) =    -13.02    dSr avg (298., 1500. K) =    -13.09
dGr  {kcal/mol}  ( " ) =     14.51    dGr avg (298., 1500. K) =     23.19
      Kc     ( " ) =   2.299E-11    Kc avg (298., 1500. K ) =  2.300E-06
The equation to the 2 parameter model of A(T)
for A(T) = Aprime * T^n
   Aprime = 1.2290E+06        n =   1.39609

THERMODYNAMIC ANALYSIS for REACTION
Rx        C3.CCOOH   = TS2
Hf {Kcal/mol}  -12.520    19.380
S {cal/mol K}  100.410    101.870

dHr {kcal/mol}   (298K) =      31.90    dHr avg (298., 1500. K) =      30.42
dU (dE) {kcal/mol} (") =      31.90    dUr avg (298., 1500. K) =      30.42
dSr {cal/mol K}  ( " ) =       1.46    dSr avg (298., 1500. K) =       -.55
dGr  {kcal/mol}  ( " ) =     31.46    dGr avg (298., 1500. K) =      30.91
      Kc     ( " ) =   8.587E-24    Kc avg (298., 1500. K ) =  3.067E-08
Fit Af/Ar     : A = 1.551E+03 n = -1.16 alpha = 7.886E-05 avg error   2.33 %
Fit Af/Ar w/ddU: A = 2.355E+05 n = -2.09 alpha =-3.871E-04 avg error   7.05 %

The equation to the 2 parameter model of A(T)
 for A(T) = Aprime * T^n
   Aprime = 4.7212E+13        n =  -.23271

THERMODYNAMIC ANALYSIS for REACTION
Rx        C3.CCOOH   = TS3
Hf {Kcal/mol}  -12.520    13.920
S {cal/mol K}  100.410    87.470

dHr {kcal/mol}   (298K) =      26.44    dHr avg (298., 1500. K) =      24.84
dU (dE) {kcal/mol} (") =      26.44    dUr avg (298., 1500. K) =      24.84
dSr {cal/mol K}  ( " ) =    -12.94    dSr avg (298., 1500. K) =    -15.05
dGr  {kcal/mol}  ( " ) =     30.30    dGr avg (298., 1500. K) =      38.37
      Kc     ( " ) =   6.153E-23    Kc avg (298., 1500. K ) =  4.704E-10
The equation to the 2 parameter model of A(T)
 for A(T) = Aprime * T^n
   Aprime = 4.4931E+10        n =  -.27610

THERMODYNAMIC ANALYSIS for REACTION
Rx        C3.CCOOH   = TS4
Hf {Kcal/mol}  -12.520    4.710
S {cal/mol K}  100.410    86.380

dHr {kcal/mol}   (298K) =      17.23    dHr avg (298., 1500. K) =      18.72
dU (dE) {kcal/mol} (") =      17.23    dUr avg (298., 1500. K) =      18.72
dSr {cal/mol K}  ( " ) =    -14.03    dSr avg (298., 1500. K) =    -12.57
dGr  {kcal/mol}  ( " ) =     21.41    dGr avg (298., 1500. K) =      30.02
      Kc     ( " ) =   2.007E-16    Kc avg (298., 1500. K ) =  5.037E-08
 The model fitted is for uni-molecular reaction.

The equation to the 2 parameter model of A(T)
for A(T) = Aprime * T^n
   Aprime = 1.6828E+04        n =  2.14073
```

Table B.13 Chemdis Input for QRRK Analysis

```
FITRANGE    (uncomment if want modified Arrhenius fits)
temp
8  298.  300. 400.  500.  600.  700.  1000.  1500.
pres
1  0.807
#NOrot   (no external rotor included)
dissoc
chemact
INPUT (A, n,alpha, E kcal k=AT^nexp(-alpha*T)exp(-E/RT) 2.65E+12 98/sehested)
 9.64E11   0.  0.  0.
#Wu, D.; Bayes, K.D.(at 300 K) Int. J. Chem. Kinet. 18, 547 (1986)
MASS
 103.07590
PARAMETERS (Anstrom, K)
 5.205       521.3
COLLIDER (take user's data if collider name started with a '!')
   N2
   1.
# EXP (temperature exponent to alpha, alpha=alpha(300)*(T/300)^N )
#  0.01
#BETA (do constant beta calculation if uncomment)
# .75
INT   (integration interval in kcal)
   0.5
WELL 1
   C3CCOOJ
     FREQ
   3    468.9       20.170
       1533.1       16.444
       3696.7        8.886
   REACTANTS
      C3CCJ+O2
      1.30E+15     0.0  0.0  32.38
      #Af= 9.64E11 0. 0. 0., Af/Ar = 7.481E-4
   ISOMER
      C3.CCOOH
      1.6104E+09     .60842   0.0  23.41
      #Afactor C3CCOOJ = TS1 (afact.lst)
   PRODUCTS
      OH + C3CC=O
      3.7077E+09    .81157   0.0  43.57
      #Afactor C3CCOOJ = TS5 (ts1.a file)
END
WELL 2
   C3.CCOOH
    FREQ
   3    399.2       17.354
       1541.0       19.912
       3999.6        7.734
   ISOMER
      C3CCOOJ
      1.2290E+06     1.39609   0.0  11.42
      #Afactor C3.CCOOH   = TS1 (afact.lst)
   PRODUCTS
      CH3 + C=C(C)COOH
      4.7212E+13    -.23271  0.0  30.42
      #Afactor C3.CCOOH   = TS2   (afact.lst)
   PRODUCTS
      C=C(C2)+CH2O+OH
      4.4931E+10    -.27610  0.0  24.84
      #Afactor C3.CCOOH   = TS3 (afact.lst)
   PRODTS
      C2CYCCOC+OH
      1.6828E+04    2.14073  0.0  18.72
      #Afactor C3.CCOOH   = TS4  (afact.lst)
END
TAG    dis
comments : 10-17-2001
```

Table B.14 Input Parameters for QRRK Calculation: C3CC· + O_2 → Products

Reaction Paths	A	n	Ea
$C_3CC\cdot+O_2 \Rightarrow C_3CCOO\cdot$	9.64E+11	0.000	0.00
$C_3CCOO\cdot \Rightarrow C_3CC\cdot+O_2$	3.73E+03	0.000	36.15
$C_3CCOO\cdot \Rightarrow OH + C_3CC{=}O$	1.23E+14	0.193	43.06
$C_3\cdot CCOOH \Rightarrow C_3CCOO\cdot$	2.86E+10	0.604	10.58
$C_3CCOO\cdot \Rightarrow C_3\cdot CCOOH$	9.66E+11	0.608	23.41
$C_3\cdot CCOOH \Rightarrow CH_3 + C{=}C(C)COOH$	4.87E+14	-1.025	29.57
$C_3\cdot CCOOH \Rightarrow C{=}C(C_2)+CH_2O+OH$	7.61E+14	-1.068	24.00
$C_3\cdot CCOOH \Rightarrow C_2CYCCOC+OH$	3.69E+09	1.349	17.88

Table B.15 Calculated Rate Constants, P = 1 atm

Reaction Paths			A	n	Ea
C3CC·+O2	<=>	C3CCOO·	6.13E+47	-11.78	9142
C3CC·+O2	<=>	C3.CCOOH	1.75E+34	-9.24	1290
C3CC·+O2	<=>	CH3 + C=C(C)COOH	4.49E+28	-5.72	17785
C3CC·+O2	<=>	C=C(C2)+CH2O+OH	1.25E+32	-6.64	15404
C3CC·+O2	<=>	C2CYCCOC+OH	1.06E+32	-5.65	14127
C3CCOO·	<=>	C3CC·+O2	1.60E+39	-11.76	44947
C3CCOO·	<=>	OH + C3CC=O	4.65E+48	-11.38	51018
C3CCOO·	<=>	C3.CCOOH	3.16E+61	-15.81	35440
C3CCOO·	<=>	CH3 + C=C(C)COOH	5.36E+59	-15.4	54288
C3CCOO·	<=>	C=C(C2)+CH2O+OH	9.42E+62	-16.22	50529
C3CCOO·	<=>	C2CYCCOC+OH	2.00E+60	-14.4	46564
C3.CCOOH	<=>	C3CCOO·	5.65E+59	-15.81	22418
C3.CCOOH	<=>	C3CC·+O2	2.41E+32	-10.12	32770
C3.CCOOH	<=>	OH + C3CC=O	3.08E+39	-9.04	37105
C3.CCOOH	<=>	CH3 + C=C(C)COOH	1.85E+33	-7.82	32159
C3.CCOOH	<=>	C=C(C2)+CH2O+OH	1.36E+35	-8.31	27236
C3.CCOOH	<=>	C2CYCCOC+OH	2.73E+32	-6.61	22192

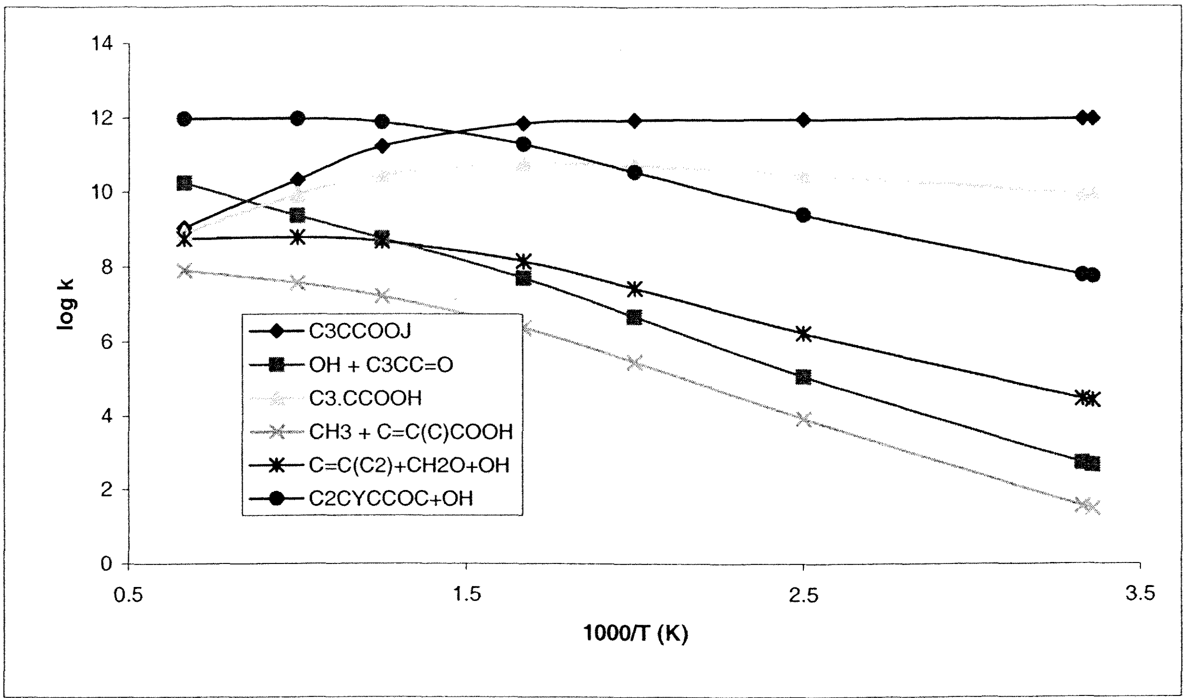


Figure B.19 QRRK Analysis of The Reaction Neopentyl and O_2 at 1 atm

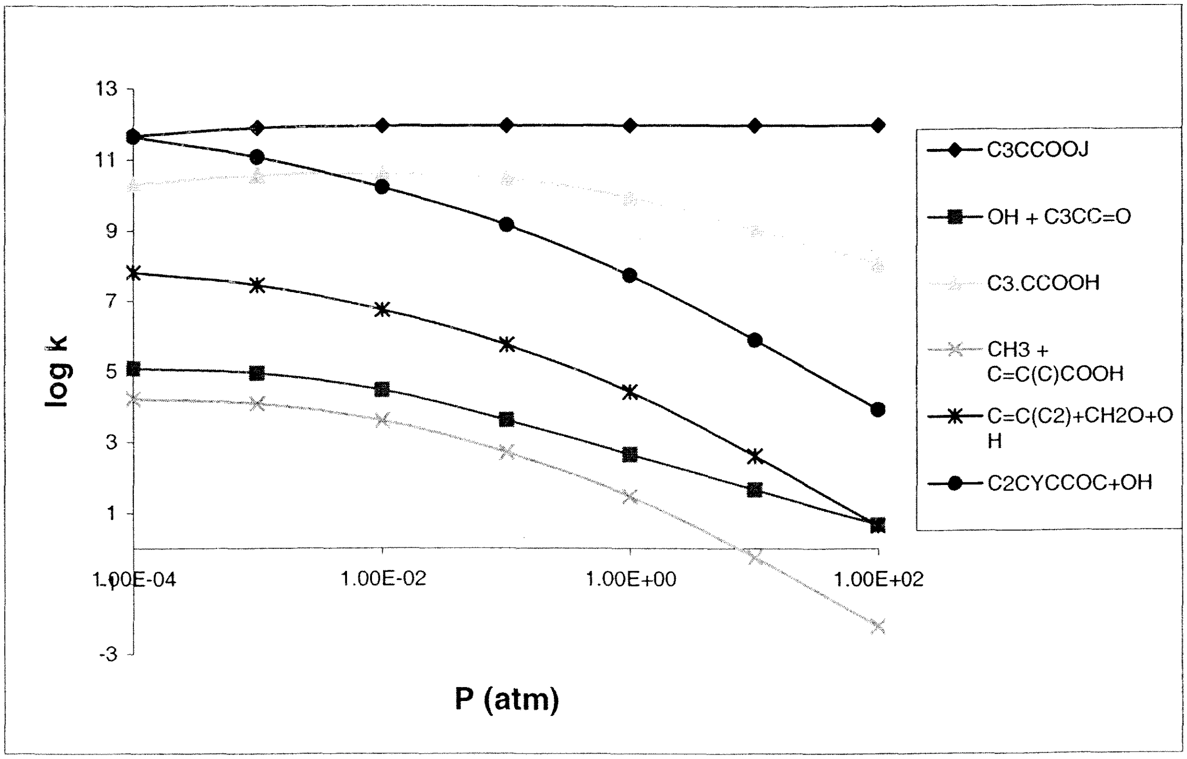


Figure B.20 QRRK Analysis of The Reaction Neopentyl and O_2 at 298 K

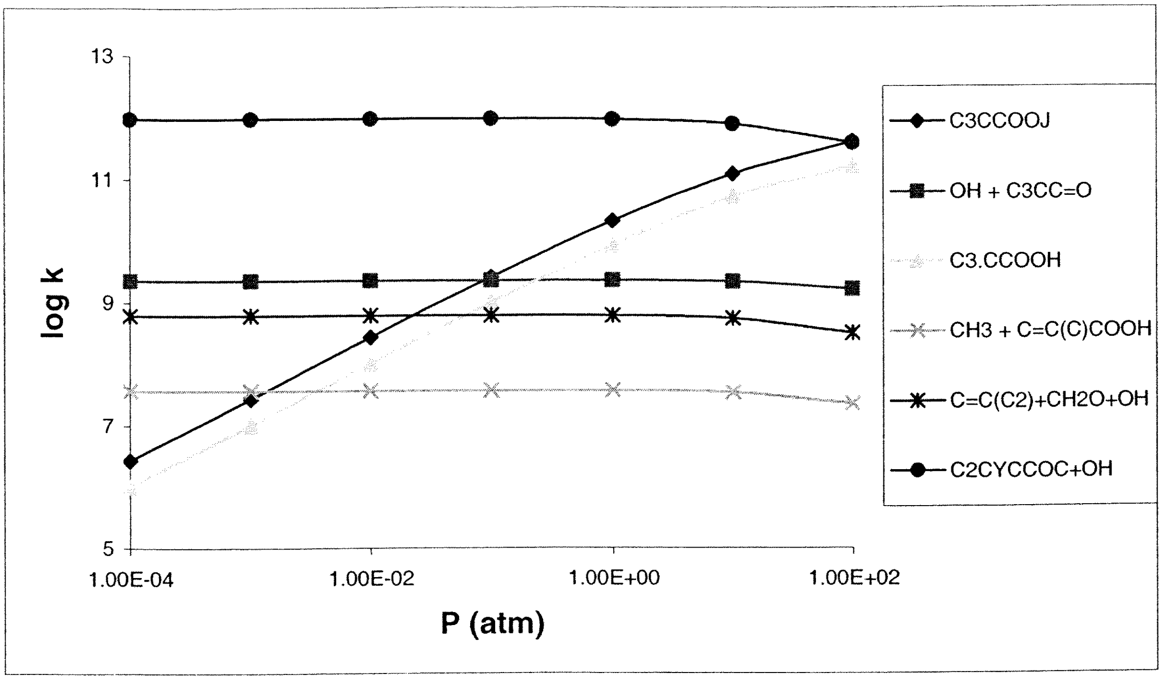


Figure B.21 QRRK Analysis of The Reaction Neopentyl and O_2 at 1000 K

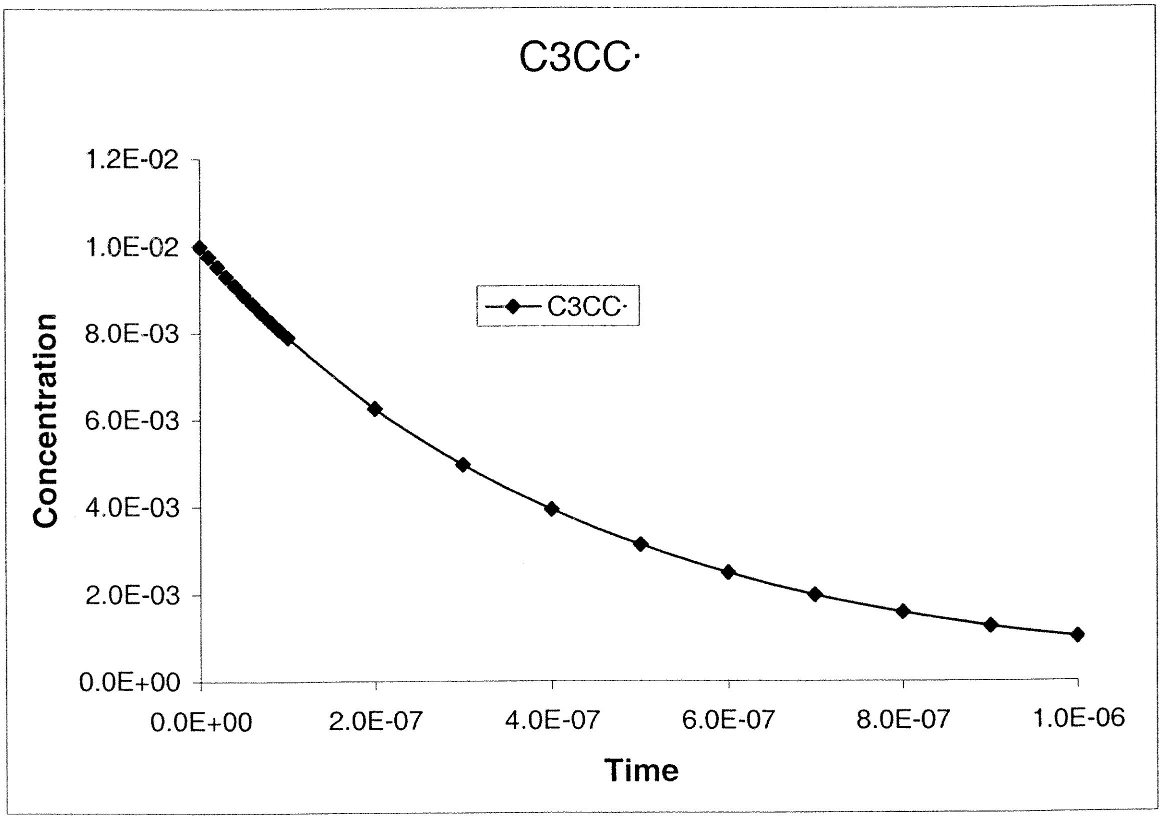


Figure B.22 $C_3CC\bullet$ Formation

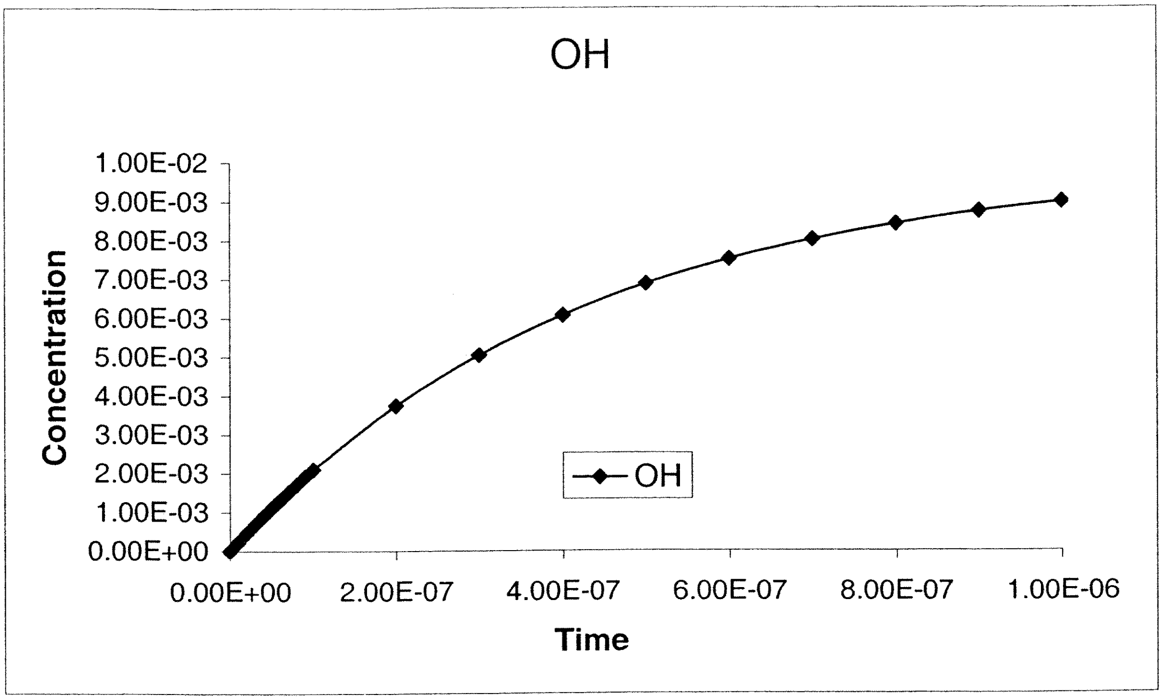


Figure B.23 OH Formation

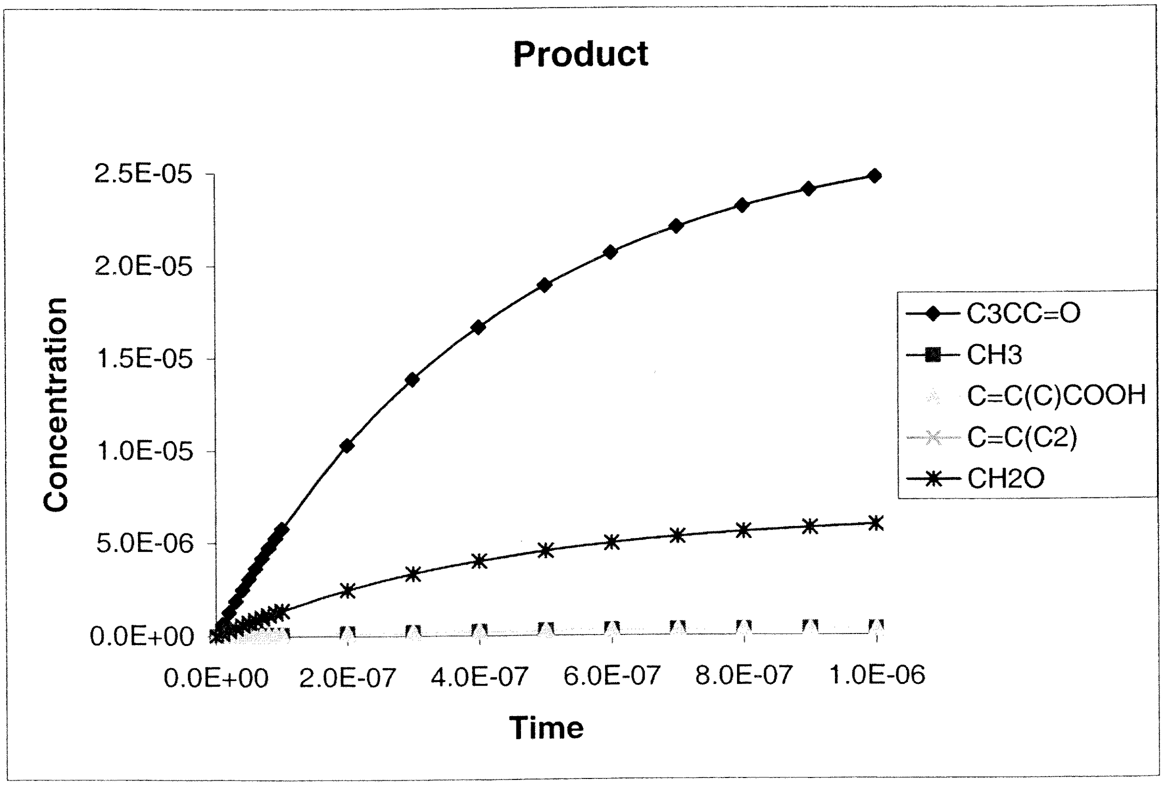


Figure B.24 Product Formation

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