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ABSTRACT

KINETICS OF HO₂ ABSTRACTION OF H ATOMS FROM HYDROCARBONS AND THERMOCHEMICAL PROPERTIES OF URETHANE MONOMERS AND RADICALS

by
Rajul Shah

SECTION I: Kinetics of HO₂ Abstraction of H Atoms From Hydrocarbons

Structures, internal rotational barriers and ideal gas thermochemical properties, ΔH_f^0 at 298 K for representative series of transition states for abstraction of H atoms from primary, secondary and tertiary hydrocarbons by the HO₂ radical, TC-HOOH (1), TCC-HOOH (2), TC₂C-HOOH (3), TC₃C-HOOH (4), TC₂CC-HOOH (5), TC₂CC-HOOHC (6) and TC₃CCC-HOOH (7) are analyzed in this study. Molecular structures and vibrational frequencies are determined at the B3LYP/6-311G(d,p) density functional level. The S^0 and $C_p(T)$ values (300 ≤ T/K ≤ 1500) from vibrational, translational, and external rotational contributions are calculated using statistical mechanics based on the vibrational frequencies and structures obtained from the density functional study. Internal rotor contributions are included in the S and $C_p(T)$ values. ΔH^\ddagger_{TS} of the transition states are computed at the G3MP2 level. The forward and reverse rate constants are calculated for the transition state reactions (1) to (7). ΔH_{rxn} of these paths are estimated. ΔH^\ddagger_{TS} of species 1, 2, 3, 4 and 5 are also calculated at CBS-Q//B3LYP/6-311G(d,p) level and compared with the G3MP2 results.

SECTION II: Thermochemical Properties, Enthalpy, Entropy and Heat Capacity (T) for Model Urethane Monomers and Corresponding Radicals

Two separate model urethanes (carbamates), Ethyl N Ethyl carbamate [C-C-N-C(O)-O-C-C] and N (n-propyl) methylcarbamate [C-C-C-N-C(O)-O-C] are utilized to investigate the thermochemical properties and bond energies in several model urethane monomers. Molecular structure, vibration frequencies, energies, enthalpies ($\Delta H_{f(298)}^0$) and bond energies are determined for the molecules and radicals at the B3LYP/6-31 G(d,p) Density Functional Calculation Level. Entropy ($S_{(298)}^0$) and heat capacity $C_p(T)$ are determined from the above structures and vibration frequencies. Enthalpies of formation ($\Delta_f H_{(298)}^0$) are estimated using total energies including zero point vibrational energy (ZPVE), thermal contributions for each species and the calculated ΔH_{rxn}^0 from isodesmic- working reactions. Bond energies are also calculated. The enthalpy values calculated at the B3LYP/6-31 G(d,p) level for C-C-N-C(O)-O-C-C and C-C-C-N-C(O)-O-C are -115.08 and -113.34 kcal/mol, respectively. Carbon and nitrogen – hydrogen bond energies, calculated in this study are: 453.2 (kJ.mol) for C-C-N_j-C(O)-O-C-C, 400.3 (kJ.mol) for C-C_j-N-C(O)-O-C-C, 430.1(kJ.mol) for C_j-C-N-C(O)-O-C-C, 429.4 (kJ.mol) for C-C-N-C(O)-O-C_j-C, 439.9 (kJ.mol) for C-C-N-C(O)-O-C-C_j, 452.7 (kJ.mol) for C-C-C-N_j-C(O)-O-C, 401.7 (kJ.mol) for C-C-C_j-N-C(O)-O-C, where j represents the radical site.

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AND THERMOCHEMICAL PROPERTIES OF URETHANE MONOMERS AND
RADICALS**

**by
Rajul Shah**

**A Thesis
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**KINETICS OF HO₂ ABSTRACTION OF H ATOMS FROM HYDROCARBONS
AND THERMOCHEMICAL PROPERTIES OF URETHANE MONOMERS AND
RADICALS**

Rajul Shah

Dr. Joseph Bozzelli, Thesis Advisor
Distinguished Professor of Chemistry, NJIT

Date

Dr. Norman Loney, Committee Member
Associate Professor of Chemical Engineering, NJIT

Date

Dr. Laurent Simon, Committee Member
Assistant Professor of Chemical Engineering, NJIT

Date

BIOGRAPHICAL SKETCH

Author: Rajul Shah
Degree: Master of Science
Date: January, 2004

Undergraduate and Graduate Education:

- Master of Science in Chemical Engineering,
New Jersey Institute of Technology, Newark, NJ, 2004
- Bachelor of Technology in Chemical Engineering,
Osmania University College of Technology, Hyderabad, India, 2001

Major: Chemical Engineering

This thesis is dedicated to my beloved family

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SECTION I

KINETICS OF HO₂ ABSTRACTION OF H ATOMS FROM HYDROCARBONS

CHAPTER 1

INTRODUCTION

Hydrogen abstraction reactions are of major interest in the chemical industry. Alkyl hydroperoxides and peroxy radicals are important intermediates in atmospheric chemistry and in low moderate temperature combustion processes. They are strongly linked to knock in spark ignition engines. There is, however, remarkably little or no data available for these peroxy and peroxide species. Their thermochemical properties – enthalpies and entropies (T) – are critical to the determination of the paths and the kinetics for their reactions. The oxidation of the hydrocarbon is initiated mainly by the reaction with hydroperoxy radical, HO₂, to produce alkyl radicals and hydrogen peroxide via H-atom abstraction from other hydrocarbon species with weakly bonded hydrogen atoms. The reaction pathway for one of the hydrocarbons studied is shown in Figure 1.1.

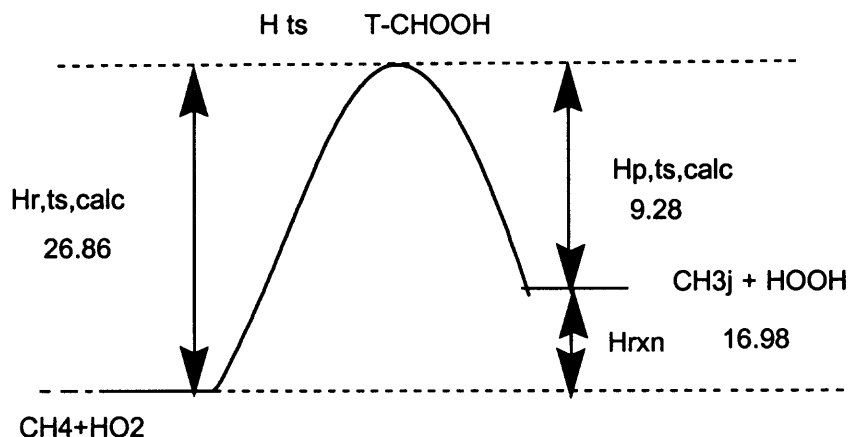


Figure 1.1 Pathway for CH₄ + HO₂ to CH₃ + HOOH. (Units in kcal/mol)

CHAPTER 2

LITERATURE SURVEY

Denisov¹, proposed an empirical method of estimation of bond dissociation energies². This method is based on experimental kinetic measurements coupled with the use of equations from a parabolic model of the transition state^{3,4}. The parabolic model treats the transition state of a reaction involving hydrogen abstraction, for example the reaction of a peroxy radical with an inhibitor, such as phenol, amine or hydroxylamine is considered



as the result of the intersection of two potential curves. One of the curves refers to the vibration of the attacked In-H bond, the other to the vibration of the forming O-H bond of the hydroperoxide. Every elementary reaction with hydrogen atom abstraction is then characterized by the following parameters:

1. The enthalpy of the reaction ΔH_e , measured as the distance between the two minimum points of the potential curves

$$\Delta H_e = D_i - D_f + 0.5hN(v_i - v_f) \quad (2.2)$$

where D_i and D_f are the dissociation energies of the In-H and ROO-H bonds respectively, v_i and v_f are their vibration frequencies, h is Plank's constant and N is Avogadro's number.

2. The activation energy of the reaction E_e , which is related to the observed E (zero point energy) by the equation: $E_e = E + 0.5hNv_i$
3. The distance of hydrogen atom transfer r_e , which is equal to the distance between the zero points of the two potential curves at the moment of forming the transition state.

4. Parameters b_i and b_f , which are the dynamic characteristics of In-H and ROO-H bonds respectively. $b_i = \pi v_i (2\mu_i)^{1/2}$, $b_f = \pi v_f (2\mu_f)^{1/2}$, Where, μ_i and μ_f are the reduced masses of the bonds transformed in the elementary act.

The parameter br_e characterizes all reactions of the same class and may be calculated from experimental data using equation (2.3), where $a = b_i/b_f$.

$$br_e = a(E_e - \Delta H_e)^{1/2} + E_e^{1/2} \quad (2.3)$$

The important characteristic of every class of hydrogen atom abstraction reaction is the activation energy of the thermoneutral reaction of the particular class when $\Delta H_e = 0$, which may be calculated using formula: $E_{eo} = (br_e)^2 (1 + a)^{-2}$.

If the parameter br_e is known, one can calculate the activation energy of any reaction of this class using the following formula⁴ (2.4)

$$E_e^{1/2} = br_e (1 - a^2)^{-2} x \left\{ 1 - a \left[1 - (br_e)^{-2} (1 - a^2) \Delta H_e \right]^{1/2} \right\} \quad (2.4)$$

When $b_i = b_f$ and $a = 1$, Equation (2.4) takes the following simple form

$$E^{1/2} = 0.5br_e + 0.5(br_e)^{-1} \Delta H_e \quad (2.5)$$

This approach was used for the estimation of the parameters of peroxy radical reactions with phenols Ar_1OH , sterically hindered phenols Ar_2OH^5 , amines AmH , hydroxylamines $AmOH$, and thiophenols, $ArSH$. The results are presented in Table 2.1. The pre-exponential factor A used in the calculation of activation energy was the same for each class of reactions.

Table 2.1 Parameters of Reaction of Peroxyl Radical with Antioxidants and Hydrocarbons: R_1H -aliphatic, R_2H -olefins, R_3H -alkylaromatic; br_e -(kcal/mol)^{1/2}, E_{eo} -kcal/mol, A -cm³/mol s

Antioxidant	br_e	α	E_{eo}	A
Ar_1OH	3.22	1.00	10.30	3.2×10^{10}
Ar_2OH	3.44	1.00	12.38	3.2×10^{10}
AmH	2.61	0.94	7.55	3.2×10^{10}
$AmOH$	3.70	1.00	14.32	3.2×10^{10}
$ArSH$	2.48	0.66	9.39	3.2×10^{10}
R_1H	3.40	0.81	14.70	1.0×10^{11}
R_2H	3.75	0.81	17.85	1.0×10^{10}
R_3H	3.52	0.81	15.77	1.0×10^{10}

Rate Expressions are also available from previous work for the HO_2 abstraction of H atoms from Hydrocarbons for some of the reactions and these values are listed in Table 2.2. These rate constants are compared with the rate constants computed in this study in Section 4.4

Table 2.2 Literature Values for Rate Constants from Previous Studies

Reaction	Literature Value (300 – 2500 K)
$CH_4 + HO_2 \rightarrow CH_3 + HOOH$	$1.81 \times 10^{11} e^{-18.58/RT}{}^6$
$C_2H_6 + HO_2 \rightarrow C_2H_5 + HOOH$	$2.95 \times 10^{11} e^{-14.94/RT}{}^6$
$CCC + HO_2 \rightarrow CC_jC + HOOH$	$2.61 \times 10^{10} e^{-13.91/RT}{}^7$
$C_3C + HO_2 \rightarrow C_3C_j + HOOH$	$7.36 \times 10^9 T^{2.55} e^{-10.53/RT}{}^8$
$C_3C + HO_2 \rightarrow C_3C_j + HOOH$	$6.14 \times 10^{10} T^{2.55} e^{-15.5/RT}{}^8$

CHAPTER 3

CALCULATION METHODS

G3(MP2)⁹ method in Gaussian 98 program suite¹⁰ is used for all calculations. G3(MP2) theory, is a modification of the G3 theory¹¹, which is much more accurate and requires less computational time and scratch space than the G2(MP2) theory¹². Both the G3(MP2) and CBS-Q theories use the B3LYP density functional method^{13,14} for geometries and zero-point energies. Durant¹⁵ has compared density functional calculations B3LYP and hybrid (BH and H) with MP2 and Hartree-Fock methods for geometry and vibration frequencies. He reports that these density functional methods provide excellent geometries and vibration frequencies, relative to MP2 at a reduced computational expense. Petersson et al.¹⁶ currently recommends the use of B3LYP for geometry and frequencies in several of his CBS calculation methods. In this study, the two theories CBS-Q and G3(MP2) are modified using the geometries and the zero-point energies obtained at the B3LYP/6-311G(d,p) level.

The optimized geometry, harmonic vibration frequencies, and zero-point vibrational energies (ZPVE) are computed at the B3LYP/6-311G(d,p) level. The optimized structure parameters are used to obtain total electronic energies at the B3LYP/6-311G(d,p), QCISD(T)/6-311G(d,p), CBSQ//B3LYP/6-311G(d,p) and G3(MP2) levels. Total energies are corrected by ZPVE's, which are scaled by 0.9806 as recommended by Scott et al¹⁷. Thermal corrections (0 K to 298 K) are calculated to estimate $\Delta H_f^0_{298}$ at 298K.¹⁸

3.1 Determination of the Enthalpy of Formation

ΔH_f^0 of the stable organic parent molecules, and most of the hydrocarbon radical products have been experimentally or theoretically determined. The literature values for enthalpy of these hydrocarbons and the HC radicals are used in the calculations of kinetic parameters. The enthalpy values used for these standard species are included in the results and discussion section. Enthalpies of the stable reactants and products are also calculated here in order to determine an accurate energy difference between these reactants / products and the energy of the saddle point transition state, which is needed in overcoming the barrier to the forward and reverse reactions.

Enthalpies of formation (ΔH_f^0), for these compounds and for transition states are calculated using the G3MP2 composite method and B3LYP/6-311G(d,p) density functionals. CBSQ composite method is also used to compute the values for selected transition states where the molecules were less than seven heavy atoms: TC-HOOH, TCC-HOOH, TC₂C-HOOH, TC₃C-HOOH and TC₂CC-HOOH. The initial structure of each compound or transition state is determined using UHF/PM3 in MOPAC¹⁹, followed by optimization and vibrational frequency calculation at B3LYP/6-311 G(d,p) level of theory using Gaussian 98¹⁰. Transition state geometries are identified by the existence of only one imaginary frequency, structure information, and the TST reaction coordinate vibration information. The following are the reactions and compounds studied (j represents a radical site):

Reaction	Type of C—H bond
1. $CH_4 + HO_2 \rightarrow TC - HOOH \rightarrow CH_3 + HOOH$	Methyl
2. $C_2H_6 + HO_2 \rightarrow TC - C - HOOH \rightarrow C_2H_5 + HOOH$	Primary

- | | |
|--|-----------|
| 3. $CCC + HO_2 \rightarrow TC_2C - HOOH \rightarrow CC_jC + HOOH$ | Secondary |
| 4. $C_3C + HO_2 \rightarrow TC_3C - HOOH \rightarrow C_3C_j + HOOH$ | Tertiary |
| 5. $C_3C + HO_2 \rightarrow TC_2CC - HOOH \rightarrow C_3_jC + HOOH$ | Primary |
| 6. $C_2CCC + HO_2 \rightarrow TC_2CC - HOOH - C \rightarrow C_2CC_jC + HOOH$ | Secondary |

The ΔH_f^0 's of the transition state structures are estimated by evaluation of ΔH_f^0 of the stable radical adducts plus the difference of total energies with ZPVE and thermal correction between these radical species and the transition state. The method is illustrated for the transition state TC-HOOH in Figure 1.1

$$\Delta H_{R,TS,calc} = \Delta H_{rxn} (\text{Reactant} \rightarrow \text{TS}) + \Delta H_f^0_{298,R's}$$

$$\Delta H_{P,TS,calc} = \Delta H_{rxn} (\text{Product} \rightarrow \text{TS}) + \Delta H_f^0_{298,P's}$$

$$\Delta H^\ddagger_{TS} = (\Delta H_{R,TS,calc} + \Delta H_{P,TS,calc}) / 2$$

Calculation of H^\ddagger for the transition state TC-HOOH is not taken as the calculated energy difference between reactant and transition state. The H^\ddagger is calculated from an average of the calculated Tst enthalpy and the calculated values of the reactants and products. $\Delta H_{R,TS,calc}$ is the difference between the calculated energy of the transition state and the reactant plus ΔH_f^0 of the reactants. $\Delta H_{P,TS,calc}$ is the difference between the calculated energy of the transition state and product plus ΔH_f^0 of the products. ΔH^\ddagger_{TS} is calculated by taking the arithmetic average of the two values $\Delta H_{R,TS,calc}$ and $\Delta H_{P,TS,calc}$. The data for these calculations is discussed in Chapter 4.

3.2 Determination of Entropy and Heat Capacity

Literature values of S^0_{298} and $C_p(T)$ for the hydrocarbons and corresponding radicals are utilized in the evaluation of kinetic parameters; these values are presented in the results and discussion. Entropy and $C_p(T)$ data are calculated for the transition state structures. The contributions of external rotation and vibrations to entropy and heat capacity are calculated from the moments of inertia of the optimized structures, and the scaled vibrational frequencies, respectively. Contributions from torsion frequencies corresponding to internal rotation are replaced with values calculated from the method of Pitzer and Gwinn²⁰ for S and $C_p(T)$. The moments of inertia of the internal rotors are calculated from the ROTATOR program, which takes the Cartesian coordinates of the atoms in the molecule, the identified rotation bond and then determines the I_x of each component of the rotor. The number of optical isomers (greater than 1) is also incorporated into the calculation of S^0_{298} .

For the transition state structures, the data for optical isomers is included in the SMCPS files for the determination of S^0_{298} and $C_p(T)$, specifically, the [H\O-O/H and H/O-O/H] structures are analyzed and determined to have 1 or no extra optical isomer forms for rotation about the HO-OH bond. These data are specified in the SMCPS input files and in the species thermochemical data files along with symmetries and foldness of the internal rotors. Scaling factor to correct the entropies and heat capacities is not used here. A computer code **THERM** (Thermo Estimation for Radicals and Molecules) for IBM PC's and PC compatibles is used to estimate the thermodynamic property data for gas phase radicals and molecules C_2CCC and C_2CC_3C using Benson's group additivity method;²³ because data for these species are not present in data compilations. The

thermodynamic properties are generated in the NASA polynomial format for compatibility with the CHEMKIN²⁴ reaction modeling code or the NASA equilibrium code.²⁵ In addition, thermodynamic, kinetic and equilibrium analysis are also performed by the code.

3.2.1 Hindered Internal Rotations

Barriers of hindered internal rotation adjacent to radical center are an important factor in determining the kinetic pre-exponential factor, because entropy is in the exponent of this canonical transition state calculation. The barriers of hindered internal rotations for the transition states considered in this work are listed in Table 4.5 along with references to the source of the corresponding value. The majority of the data on rotational barriers in Table 4.5 are results of experimental determinations or *ab initio* quantum mechanic calculations in literature. When literature data are not available, the barriers are assigned by interpolation of the values from similar, studied internal rotor systems. The method and tables of Pitzer and Gwinn^{20,21,22} are then used to calculate the contribution of hindered internal rotations to the thermodynamic functions.

3.3 High-Pressure Limit A Factor (A_∞) and Rate Constant (k_∞) Determination

Entropy differences between reactants and transition states are used to determine the Arrhenius pre-exponential factor, A_∞ , via canonical transition state theory²⁶ (TST) for bimolecular reactions, $A_\infty = (ekT/h) \exp(\Delta S^\ddagger / R)$, where, h is the Plank's constant, and k is the Boltzmann constant. The barrier (activation energy) is calculated from the difference in enthalpies of formation of the reactants and the transition state.

The high pressure limit rate constants (k_{∞} 's) of HO₂ abstraction reactions are fit by three parameters A_{∞} , n , and E_a over temperature range from 298 to 2000 K:

$$k_{\infty} = A_{\infty}(T)^n \exp(-E_a/RT)$$

The calculations for the three parameter fit for the determination of the high pressure rate constants are shown in Chapter 4 – part 4. The entropies and heat capacities for the reactants, transition states and radical products used in the calculations are presented in Table 4.4

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Structures and Vibration Frequencies of Molecules and Radicals

Illustrations of the optimized geometries at the B3LYP/6-311G(d,p) density functional calculation level for the molecules, transition states and radicals, along with structural parameters, vibration frequencies and moments of inertia are presented in tables and figures in Appendix A.1 The cleaving C-H bond length in the transition state for HO₂ abstraction from CH₄, TC-HOOH, is 1.441 Å as shown in Figure 4.1 and the forming H-O bond is 1.111 Å. The O-OH bond length also changed from 1.328 Å to 1.415 Å.

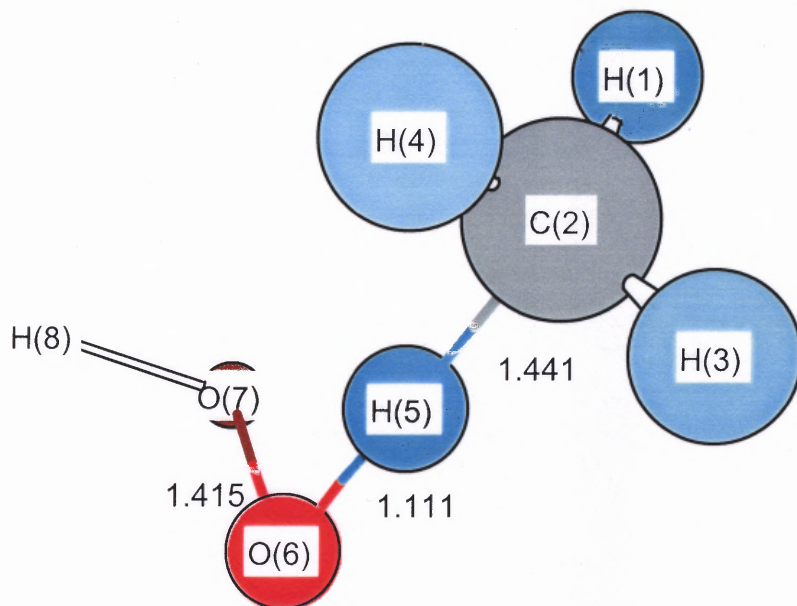


Figure 4.1 Geometry of the Transition State TC-HOOH (Units: Angstroms).

The figures illustrating the structures of the remaining transition states (Figure A.1 - Figure A.6) are shown in Appendix A.2. The cleaving C-H bond length in the

transition state for the primary C-H bond in ethane TCC-HOOH is 1.395\AA , the forming H-O bond is 1.145\AA and the O-OH bond length is 1.415\AA . The cleaving C-H bond length in the transition state for the secondary carbon in propane, TC₂C-HOOH, is 1.364\AA , the forming H-O bond is 1.171\AA and the O-OH bond length is 1.414\AA . The cleaving C-H bond length in the transition state for the tertiary C-H bond isobutene, TC₃C-HOOH, is 1.337\AA , the forming H-O bond is 1.197\AA and the O-OH bond length is 1.413\AA . The cleaving C-H bond length in the transition state for the primary C-H bond in isobutene, TC₂CC-HOOH, is 1.395\AA , the forming H-O bond is 1.146\AA and the O-OH bond length is 1.416\AA . The cleaving C-H bond length in the transition state for the secondary C-H bond in 2methylbutane, TC₂CC-HOOHC, is 1.367\AA , the forming H-O bond is 1.174\AA and the O-OH bond length is 1.415\AA .

4.2 Enthalpies to the Transition States

Enthalpies of the transition states are estimated using total energies calculated by the CBS-Q and G3(MP2) theories. The total energies of all the species are from structures optimized at the B3LYP/6-311 G(d,p) level and are presented in Table 4.2

For example, $\Delta H_{f, 298}^0$ of the transition state TC-HOOH can be calculated from Reaction 1, which can be written (separately for the two directions, forward and reverse) as:



$$\Delta H_{298 \text{ to } \text{tst}} = \sum(\text{total energies})_{298} \text{ at saddle point } \text{tst} - \sum(\text{total energies})_{298} \text{ of reactants}$$

This data is taken from the calculations of the reactants, products and the transition state structures – Table 4.2. The calculated $\Delta\Delta H_{f(298)}$ from the TS structure to the reactants for $\text{CH}_4 + \text{HO}_2$ is 26.86 kcal/mol. The calculated $\Delta\Delta H_{f(298)}$ from the transition state structure to the products $\text{H}_2\text{O}_2 + \text{CH}_3$ is 9.28 kcal/mol. These two $\Delta\Delta H_{f(298)}$ values are now used to determine an enthalpy value for the transition state relative to the literature values (table 4.1) for the reactants and the products. The $\Delta H_{f(298)}^0$ for CH_4 is -17.89 and for HO_2 is 3.2 resulting in a combined value of -14.69 kcal/mol for reactants. The $\Delta H_{f(298)}$ for the products is $-32.53 + 34.82 = 2.29$ kcal/mol. Adding 26.86 to -14.69 results in a value of 12.17 kcal/mol for the enthalpy of the TS structure. Adding 9.28 to 2.29 results in a value of 11.57 kcal/mol for the enthalpy of the TS structure. The arithmetic average of the values 12.17 and 11.57, which is 11.87 kcal/mol is taken as the enthalpy of the TS structure TC-HOOH.

The $\Delta H_{f(298)}^0$ for all other H abstraction by HO_2 radical transition states are calculated in a similar manner. The differences in the enthalpies used to find the barrier (Table 4.3) are computed at the G3MP2 level for all the transition states. The evaluated enthalpies to the transition states and $\Delta H_{f(298)}^0$ of the transition states are listed in Table 4.4 CBS-Q calculations were also performed for some transition states based on geometry optimization with the same basis set B3LYP/6-311G(d,p) as in the G3MP2 calculations. $\Delta H_{f(298)}^0$ obtained from the CBSQ calculations for TC-HOOH (TS1) is 6.67 kcal/mol. This result is 5.2 kcal/mol lower than the corresponding G3MP2 calculated value.

Table 4.1 Enthalpies of Formation for Reference Species

Species	ΔH^0_{f298} (in kcal/mol)
CH ₄	-17.89 ²⁷
CH ₃	34.821 ²⁷
OOH	3.3±0.8 ²⁸
HOOH	-32.53 ²⁷
C ₂ H ₆	-20.04±0.07 ²⁹
C ₂ H ₅	28.4±0.5 ³⁰
CCC	-25.02±0.12 ²⁹
CC _j C	22.0±0.5 ³⁰
C ₃ C	-32.5 ³¹
C ₃ C	-32.42 ± 0.13 ³²
C ₃ C _j	11.0 ³¹
C ₃ C _j	11.0±0.7 ³⁰
C _{3j} C	17.0±0.5 ³⁰
C ₂ CCC	-37.43 ³¹
C ₂ CCC	-36.84 ± 0.23 ³³
C ₂ CC _j C	8.92 ³¹

Table 4.2 Total Energy^a, ZPVE, and Thermal Corrections from Calculations

Species	ZPVE ^b	Sum of elec ^c	Sum of zpe ^d	Thermal Corr ^e	ZPE ^f	Total Energy ^g
HO ₂	0.014112	-150.936292	-150.932489	2.39	8.68	-150.9327629
HOOH	0.026452	-151.565403	-151.561196	2.64	16.28	-151.567085
CH ₄	0.044578	-40.489165	-40.485352	2.39	27.43	-40.48621661
CH ₃	0.029574	-39.824184	-39.820172	2.52	18.20	-39.82074504
C ₂ H ₆	0.074362	-79.781898	-79.777465	2.78	45.76	-79.77890732
C ₂ H ₅	0.05873	-79.124818	-79.120607	2.64	36.14	-79.12174606
CCC	0.102986	-119.0777	-119.072209	3.45	63.37	-119.0742074
CC _j C	0.087508	-118.42665	-118.420501	3.86	53.85	-118.4221989
C ₃ C	0.130993	-158.374895	-158.368241	4.18	80.60	-158.3707826
C ₃ C _j	0.115917	-157.728424	-157.721088	4.60	71.33	-157.723337
C _{3j} C	0.115974	-157.716734	-157.709693	4.42	71.36	-157.7119434
C ₂ CCC	0.159361	-197.669262	-197.661268	5.02	98.06	-197.66436
C ₂ CC _j C	0.144401	-197.018008	-197.009476	5.35	88.86	-197.012277
T CHOOH ^h	0.054996	-191.389023	-191.382582	4.04	33.84	-191.3836496
T CCHOH	0.084468	-230.689674	-230.682248	4.66	51.98	-230.6838868
T C ₂ C-HOOH	0.112792	-269.990793	-269.981949	5.55	69.41	-269.9841373
T C ₃ CHOH	0.14071	-309.292425	-309.282142	6.45	86.58	-309.2848718
T C ₂ CCHOH	0.141076	-309.283005	-309.273066	6.24	86.81	-309.2758031
T C ₂ CCHOHC	0.169222	-348.582468	-348.57099	7.20	104.13	-348.5742734

^aOptimized at the B3LYP/6-311G(d,p) level of theory, ^bZPVE : Zero Point Correction in Hartree/Particle, ^cSum of elec = Sum of electronic and zero-point energies in kcal/mol, ^dSum of zpe = Sum of electronic and thermal enthalpies, ^eThermal Corr: Thermal Corrections in Hartree, ^fscaled zero-point energies in kcal/mol (scaled by 0.9806), ^gB3LYP/6-311G(d,p). Total Energies are in Hartree at 0 K; Unit in Hartree = 627.51 kcal/mol. ^hT represents the transition state and j represents the radical site. The total energies are used in the enthalpy calculations.

Table 4.3 Barriers to the Transition States from Forward and Reverse Reactions (Units in kcal/mol) Calculated from G3MP2 Calculations and CBSQ Calculations

Reaction (forward, reverse)	Barrier (G3MP2)	Barrier (CBSQ)	ΔH_{rxn} (298K) forward reaction kcal/mol
1. $CH_4 + HO_2 \rightarrow TCHOOH$ $CH_3 + HOOH \rightarrow TCHOOH$	26.86 9.28	21.55 4.18	16.98
2. $C_2H_6 + HO_2 \rightarrow TCCHOOH$ $C_2H_5 + HOOH \rightarrow TCCHOOH$	24.56 10.81	17.07 3.92	12.71
3. $CCC + HO_2 \rightarrow TC_2CHOOH$ $CC_jC + HOOH \rightarrow TC_2CHOOH$	23.32 11.50	13.99 3.13	11.29
4. $C_3C + HO_2 \rightarrow TC_3CHOOH$ $C_3C_j + HOOH \rightarrow TC_3CHOOH$	22.19 11.80	10.87 1.76	8.67
5. $C_3C + HO_2 \rightarrow TC_2CCHOOH$ $C_3_jC + HOOH \rightarrow TC_2CCHOOH$	27.32 12.37	16.59 2.35	13.27
6. $C_2CCC + HO_2 \rightarrow TC_2CCHOHC$ $C_2CC_jC + HOOH \rightarrow TC_2CCHOHC$	25.98 13.76	N/A	10.62

Table 4.4 Enthalpies of Transition States from G3MP2 and CBSQ Calculations (Units in kcal/mol)

Transition State (TS)	ΔH^{\ddagger}_{TS} (G3MP2)	ΔH^{\ddagger}_{TS} (CBSQ)
1. TC-HOOH	11.87	6.67
2. TCC-HOOH	7.20	0.01
3. TC ₂ C-HOOH	1.23	-7.62
4. TC ₃ C-HOOH	-7.97	-18.65
5. TC ₂ CC-HOOH	-2.82	-13.20
6. TC ₂ CC-HOOHC	-9.07	N/A

4.3 Entropy and Heat Capacity

Contributions to S^0_{298} and $C_p^0(T)$ of species from translations, vibrations, and external rotation are calculated based on vibration frequencies and moments of inertia of the optimized structures using the “SMCPS” program.³⁴ This program utilizes the rigid-rotor-harmonic-oscillator approximation from the frequencies along with moments of inertia based on the optimized B3LYP/6-311G(d,p) structures. The input values for SMCPS are given in Appendix A.6

The S^0_{298} and $C_p^0(T)$ values are listed in Table 4.5 Contributions from internal rotation for S^0_{298} and $C_p(T)$'s are calculated based on rotational barrier heights, moments of inertia of the rotors using the method of Pitzer and Gwinn²⁰, data on these parameters are listed in Table 4.6 with internal rotor contributions noted in Table 4.7 for the two methods of calculation.

Table 4.5 Ideal Gas-phase Thermodynamic Properties^a

Species	$\Delta H_f^\circ_{298}$	S°_{298}	C_p° (T)						
			300	400	500	600	800	1000	1500
CH ₄ ^e	-17.90	44.49	8.53	9.68	11.08	12.48	15.04	17.16	20.69
CH ₃ ^e	34.82	46.38	9.26	10.05	10.82	11.54	12.89	14.09	16.29
C ₂ H ₆ ^f	-20.20	54.81	12.52	15.73	18.64	21.26	25.71	29.21	34.71
C ₂ H ₅ ^f	28.50	59.51	11.64	14.53	17.07	19.30	22.98	25.80	30.27
CCC ^f	-25.33	64.50	17.88	22.63	27.05	30.93	37.11	41.88	49.36
CC _j C ^f	21.02	70.31	16.38	20.30	23.95	27.54	33.36	37.43	44.16
C ₃ C ^f	-32.5	70.43	23.11	29.52	35.37	40.42	48.37	54.36	63.92
C ₃ C _i ^f	11.70	75.67	22.33	27.04	31.82	36.27	43.62	49.34	58.53
C _{3j} C ^f	16.5	77.40	22.34	28.16	33.46	38.02	45.21	50.62	59.26
C ₂ CCC ^f	-37.43	82.03	28.61	36.47	43.62	49.77	59.44	66.70	78.12
C ₂ CC _j C ^f	8.92	86.47	27.11	34.14	40.52	46.38	55.69	62.25	72.92
HOOH ^e	-32.53	55.66	10.33	11.58	12.56	13.31	14.30	15.02	16.33
HO ₂ ^e	3.20	54.38	8.35	8.91	9.48	9.98	10.77	11.36	12.35
TCHOH ^{b,c,d}	11.87	73.17	18.04	20.81	23.24	25.28	28.45	30.83	34.73
TCCHOH ^{b,c,d}	7.20	83.78	22.38	26.71	30.56	33.81	38.91	42.72	48.76
TC ₂ CHOH ^{b,c,d}	1.23	91.80	27.91	33.50	38.54	42.85	49.67	54.78	62.85
TC ₃ CHOH ^{b,c,d}	-7.97	98.01	33.74	41.01	47.44	52.84	61.21	67.45	77.26
TC ₂ CCHOH ^{b,c,d}	-2.82	100.7	33.28	40.93	47.57	53.05	61.45	67.62	77.33
TC ₂ CCHOHC ^{b,c,d}	-9.07	107.6	38.79	47.72	55.55	62.08	72.19	79.67	91.42

a: $\Delta H_f^\circ_{298}$ in kcal/mol, S°_{298} and C_p° (T) in cal/mol.K;

b: Calculated in this study at the B3LYP-6-311G(d,p) level of calculation.

c: The S and C_p values include the contributions from translations, vibrations, external rotations, and internal rotations, d: T represents the transition state. j represents a radical site. e: Jannaf, f: computed from THERM²³

Table 4.6 Moments of Inertia (amu \AA^2) and Rotational Barriers (kcal/mol) for Internal Rotors of Transition States

Transition State (TS)	Rotor	I_A^a	I_B^a	V	n^e
TCHOOH	C-HOOH	3.406	34.31	1.0 ^b	3
TCCHOOH	C-CHOOH	3.15	270.17	2.8	3
	CC-HOOH	39.36	38.36	1.0 ^b	3
TC ₂ CHOOH	C-CCHOOH	3.15	303.28	2.8 ^c	3
	CC-CHOOH	3.15	235.47	2.8 ^c	3
	CCC-HOOH	76.15	35.52	1.0 ^b	3
TC ₃ CHOOH	C ₃ -CHOOH	3.16	338.98	3.5 ^c	3
	C ₃ -CHOOH	3.15	263.94	3.5 ^c	3
	C ₃ -CHOOH	3.16	337.71	3.5 ^c	3
	C ₃ C-HOOH	114.79	37.18	1.0 ^b	3
TC ₂ CCHOOH	C ₂ -CCHOOH	3.16	144.32	3.87 ^d	3
	C ₂ -CCHOOH	3.16	445.80	3.87 ^d	3
	C ₂ C-CHOOH	274.8	73.98	3.1 ^c	3
	C ₂ CC-HOOH	178.2	37.43	1.0 ^b	3
TC ₂ CCHOOHC	C ₂ -CCHOOHC	3.15	596.17	3.87 ^d	3
	C ₂ -CCHOOHC	3.15	667.11	3.87 ^d	3
	C ₂ C-CHOOHC	72.78	237.8	3.1 ^c	3
	C ₂ CCHOOH-C	3.15	421.04	2.8 ^c	3
	C ₂ CC-HOOHC	274.2	35.33	1.0 ^b	3

^aMoments of inertia are computed from ROTATOR, ^bcalculated using MMFF, ^cestimated value, ^dReference 35 ^en is the foldness. All calculations are at B3LYP/6-311G(d,p) level of calculation.

Table 4.7 Calculation of S°_{298} and $C_p^{\circ}(T)$ Contribution from Internal Rotors by two methods.

		S°_{298}	C_{p300}	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
c-hooh	P&G ^a	5.456	1.480	1.311	1.208	1.148	1.084	1.054	1.022
	ROT ^b	5.747	0.993	0.993	0.993	0.993	0.993	0.993	0.993
c-chooh	P&G	4.488	2.165	2.123	1.967	1.807	1.555	1.395	1.19
	ROT	5.752	0.993	0.993	0.993	0.993	0.993	0.993	0.99
cc-hooh	P&G	7.260	1.529	1.335	1.221	1.157	1.089	1.057	1.02
	ROT	7.571	0.993	0.993	0.993	0.993	0.993	0.993	0.98
c-cchooh	P&G	4.489	2.166	2.123	1.967	1.807	1.555	1.395	1.19
	ROT	5.755	0.993	0.993	0.993	0.993	0.993	0.993	0.99
ccc-hooh	P&G	7.478	1.531	1.336	1.221	1.157	1.089	1.057	1.02
	ROT	7.790	0.993	0.993	0.993	0.993	0.993	0.992	0.96
c3-chooh	P&G	4.215	2.112	2.203	2.143	2.018	1.755	1.560	1.29
	ROT	5.757	0.993	0.993	0.993	0.993	0.993	0.993	0.99
c3c-hooh	P&G	7.625	1.532	1.336	1.221	1.157	1.089	1.057	1.02
	ROT	7.937	0.993	0.993	0.993	0.993	0.992	0.988	0.94
c2-cchooh	P&G	4.086	2.064	2.205	2.192	2.095	1.854	1.649	1.35
	ROT	5.744	0.993	0.993	0.993	0.993	0.993	0.993	0.99
c2c-chooh	P&G	7.178	2.327	2.278	2.125	1.953	1.671	1.479	1.23
	ROT	8.663	0.993	0.992	0.987	0.973	0.916	0.830	0.60
c2cc-hooh	P&G	7.721	1.532	1.336	1.222	1.158	1.089	1.057	1.02
	ROT	8.033	0.993	0.993	0.993	0.993	0.991	0.983	0.91
c2-cchoohc	P&G	4.098	2.066	2.207	2.193	2.096	1.854	1.649	1.35
	ROT	5.759	0.993	0.993	0.993	0.993	0.993	0.993	0.99
c2c-choohc	P&G	7.134	2.326	2.277	2.125	1.953	1.671	1.479	1.23
	ROT	8.618	0.993	0.992	0.988	0.978	0.928	0.850	0.63
c2cchooh-c	P&G	4.492	2.166	2.124	1.968	1.807	1.555	1.395	1.19
	ROT	5.755	0.993	0.993	0.993	0.993	0.993	0.993	0.99
c2cc-hoohc	P&G	7.733	1.532	1.336	1.222	1.158	1.089	1.057	1.02
	ROT	8.045	0.993	0.993	0.993	0.993	0.991	0.983	0.91

^aPitzer and Gwinn¹⁶ ^bROTATOR

The barrier for RC-HOOH, which is 1.0, is calculated using Molecular Mechanics Force Field (MMFF) in Spartan. The S°_{298} and $C_p(T)$ values of the stable molecules and product radicals are calculated from THERM²³. The THERM data are used in the calculations here and are listed in Table 4.5. The data from the Pitzer and Gwinn method listed in Table 4.7 is used in the calculations in this study.

4.4 Pre-exponential A factor and the Equilibrium Constant K_{eq}

The rate coefficients are expressed in the modified Arrhenius form:

$$k = AT^n \exp\left(\frac{-E_a}{RT}\right) \quad (4.3)$$

where, T is the temperature in K, R = 1.987 cal/mol. K, E_a is the relative enthalpy in kcal/mol and A is pre-exponential factor in sec^{-1} . The three parameters A, n and E_a are listed in Table 4.8 and the rate constants k are estimated as per the equation (4.3) above.

A sample Thermkin calculation for the transition state T C-HOOH, calculated at the G3MP2 level of theory is shown in Table 4.9 while the remaining are presented in Appendix A.3 These are for reactions in the forward as well as reverse directions. Thermkin calculations are also performed for some of the reactions at the CBSQ level of calculation. The results from CBSQ calculations are described in Appendix A.4

Table 4.8 High-pressure Limit Rate Constants for Forward and Reverse Reactions

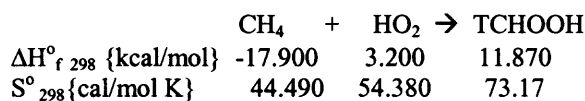
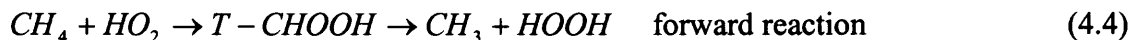
$$k = A(T/K)^n \exp(-E_a / RT) (298 \leq T/K \leq 2000) \quad (4.3)$$

Forward Reaction	A (cm ³ /mol s)	n	E _a (G3MP2) (kcal/mol)	E _a (CBSQ) (kcal/mol)
k ₁ CH ₄ + HO ₂ → T CHOOH	1.22 x 10 ³	3.202	25.81	20.60
k ₂ C ₂ H ₆ + HO ₂ → T CCHOOH	4.67 x 10 ²	3.355	23.30	16.11
k ₃ CCC + HO ₂ → T C ₂ CHOOH	7.14 x 10 ³	2.85	22.89	14.04
k ₄ C ₃ C + HO ₂ → T C ₃ CHOOH	3.18 x 10 ³	3.007	20.82	10.14
k ₅ C ₃ C + HO ₂ → T C ₂ CCHOOH	6.86 x 10 ³	3.084	25.89	15.51
k ₆ C ₂ CCC + HO ₂ → T C ₂ CCHOOHC	1.72 x 10 ³	2.947	24.66	N/A

k₁, k₂, k₃, k₄, k₅, k₆ fitting with three-parameter modified Arrhenius equation over the temperature range of 300 to 2000 K using THERMKIN (A canonical transition state calculation for the rate constant from the thermochemical data on the reactants and corresponding transition state);^{34,36} this is shown in table 4.7.

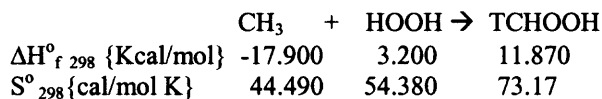
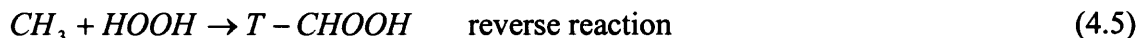
Reverse Reaction	A (cm ³ /mol s)	n	E _a (G3MP2) (kcal/mol)	E _a (CBSQ) (kcal/mol)
k ₁ CH ₃ + HOOH → T CHOOH	2.74 x 10 ⁴	2.445	9.03	3.82
k ₂ C ₂ H ₅ + HOOH → T CCHOOH	2.88 x 10 ²	2.954	10.46	3.27
k ₃ CC _j C + HOOH → T C ₂ CHOOH	6.15 x 10 ¹	3.007	12.07	3.22
k ₄ C ₃ C _j + HOOH → T C ₃ CHOOH	4.43 x 10 ⁰	3.456	11.90	1.22
k ₅ C ₃ C + HOOH → T C ₂ CCHOOH	4.41 x 10 ²	2.843	12.63	2.24
k ₆ C ₂ CC _j C + HOOH → T C ₂ CCHOOHC	2.90 x 10 ¹	3.103	13.85	N/A

k₁, k₂, k₃, k₄, k₅, k₆ fitting with three-parameter modified Arrhenius equation over the temperature range of 300 to 2000 K using THERMKIN (A canonical transition state calculation for the rate constant from the thermochemical data on the reactants and corresponding transition state);^{34,36} this is shown in table 4.8.

Table 4.9 THERMKIN Calculation (G3MP2 level of calculation)

$$A_{\text{prime}} = 1.2160E+03 \quad n = 3.20208 \quad E_a = 2.5812E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	kcalc (cm ³ /mol s)	kfit (cm ³ /mol s)
300.00	2.657E+01	-2.569E+01	1.040E+11	1.631E-08	1.626E-08
400.00	2.674E+01	-2.523E+01	2.612E+11	2.062E-03	2.054E-03
500.00	2.697E+01	-2.471E+01	5.336E+11	2.761E+00	2.778E+00
600.00	2.723E+01	-2.423E+01	9.567E+11	3.743E+02	3.784E+02
800.00	2.779E+01	-2.342E+01	2.404E+12	2.121E+05	2.132E+05
1000.00	2.830E+01	-2.285E+01	4.911E+12	1.128E+07	1.121E+07
1200.00	2.873E+01	-2.246E+01	8.805E+12	1.774E+08	1.751E+08
1500.00	2.926E+01	-2.206E+01	1.799E+13	3.153E+09	3.118E+09
2000.00	3.002E+01	-2.163E+01	4.520E+13	6.722E+10	6.827E+10



$$A_{\text{prime}} = 2.7443E+04 \quad n = 2.44553 \quad E_a = 9.0351E+03$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	kcalc (cm ³ /mol s)	kfit (cm ³ /mol s)
300.00	9.577E+00	-2.888E+01	1.03962E+11	7.902E+03	8.197E+03
400.00	9.455E+00	-2.923E+01	2.61179E+11	7.600E+05	7.326E+05
500.00	9.405E+00	-2.935E+01	5.33644E+11	1.273E+07	1.228E+07
600.00	9.416E+00	-2.933E+01	9.56745E+11	8.881E+07	8.733E+07
800.00	9.579E+00	-2.910E+01	2.40359E+12	1.152E+09	1.174E+09
1000.00	9.869E+00	-2.878E+01	4.91104E+12	6.103E+09	6.313E+09
1200.00	1.022E+01	-2.846E+01	8.80477E+12	2.038E+10	2.104E+10
1500.00	1.077E+01	-2.805E+01	1.79900E+13	7.669E+10	7.747E+10
2000.00	1.166E+01	-2.754E+01	4.51956E+13	3.481E+11	3.340E+11

The calculations for the remaining molecules follow in Appendix A.3. The gas-phase equilibrium constant at 300 K is calculated from:

$$\Delta G^{\circ} = \Delta H^{\circ} - T * \Delta S = -RT \ln K_{eq}$$

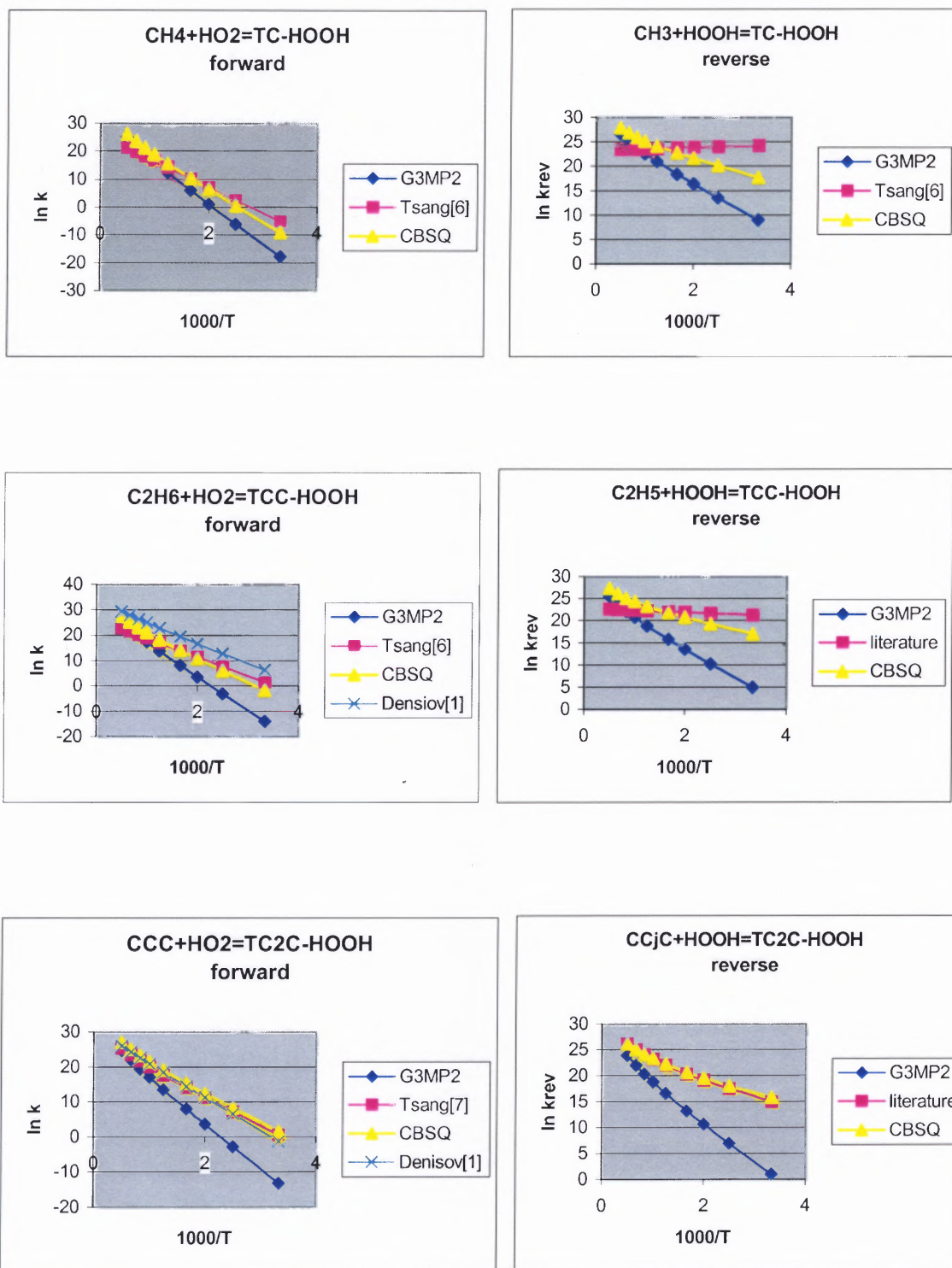
The K_{eq} values for the reactions are listed in Table 4.10

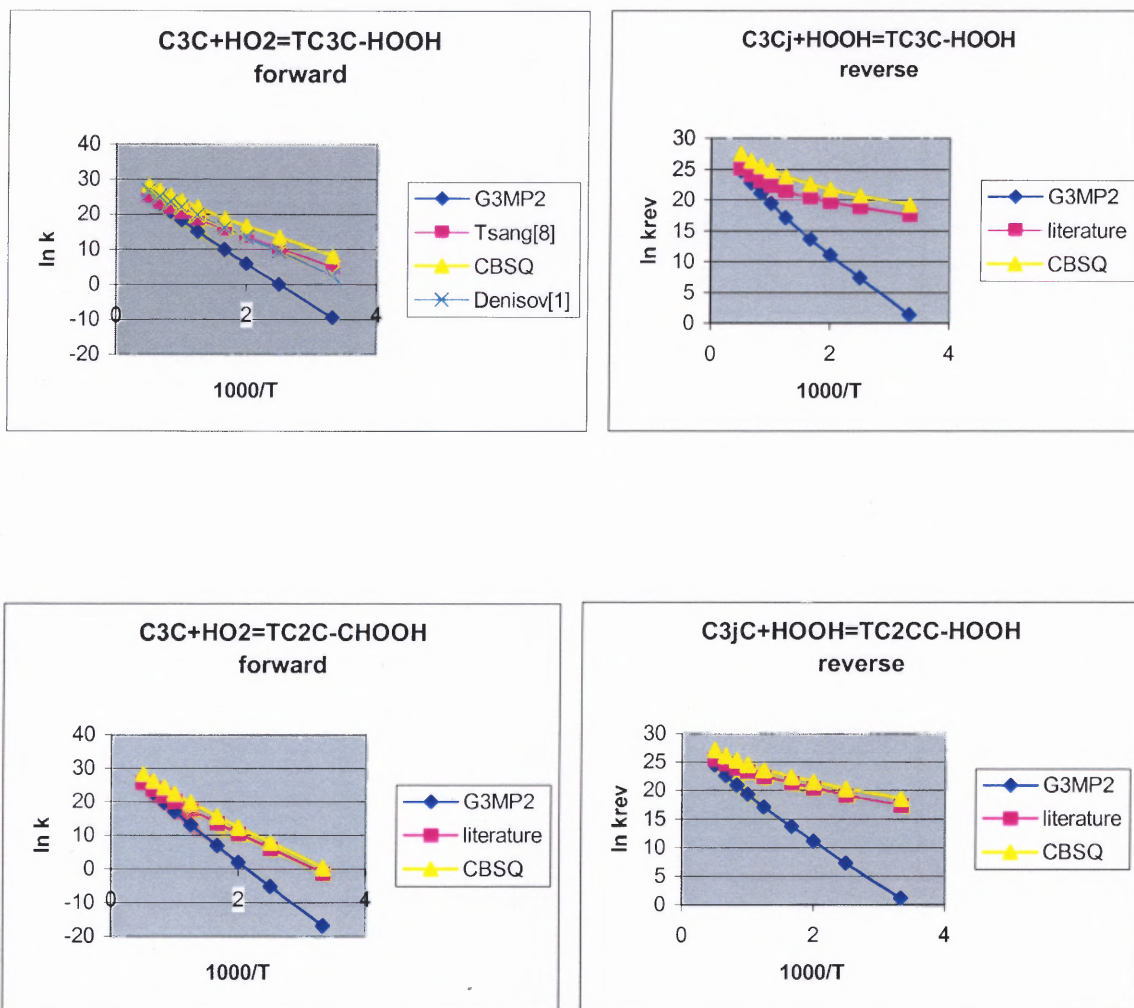
Table 4.10 Equilibrium Constants

Reaction	K_{eq} at 300K
1. $\text{CH}_4 + \text{HO}_2 \rightarrow \text{CH}_3 + \text{HOOH}$	2.064E-12
2. $\text{C}_2\text{H}_6 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5 + \text{HOOH}$	7.205E-09
3. $\text{CCC} + \text{HO}_2 \rightarrow \text{CC}_j\text{C} + \text{HOOH}$	6.491E-07
4. $\text{C}_3\text{C} + \text{HO}_2 \rightarrow \text{C}_3\text{C}_j + \text{HOOH}$	1.795E-05
5. $\text{C}_3\text{C} + \text{HO}_2 \rightarrow \text{C}_3\text{C} + \text{HOOH}$	1.365E-08
6. $\text{C}_2\text{CCC} + \text{HO}_2 \rightarrow \text{C}_2\text{CC}_j\text{C} + \text{HOOH}$	3.258E-07

The forward and reverse rate constants are computed for some of the hydrogen abstraction reactions by the G3MP2 and CBSQ calculation methods and these values are compared with those available in literature (k_{lit}) as discussed in Table 2.2. Plots are made for $\ln(k)$ versus $1000/T$ where T is the temperature in Kelvin and k_{fwd} is the forward reaction rate constant and k_{rev} is the reverse reaction rate constant. Figure 4.2 presents the comparison plots for rate constants from literature and those computed by the G3MP2 and CBSQ methods in this study. The data for the rate constant values at different temperatures from literature follow in Appendix A.5, while those from G3MP2 and CBSQ methods are presented in Appendix A.3 and A.4.

Figure 4.2 Plots of Rate Constants Calculated (k_{calc}) and From Literature (k_{lit}) vs T





The values for k_{calc} from G3MP2 calculation method are listed in Table 4.8 and Appendix A.3, while those from CBSQ method are listed in Appendix A.4 and the literature values^{1,6,7,8} obtained for the rate constants at the corresponding temperature are presented in Appendix A.5. The unit for Temperature is K, and that for the rate constant is $\text{cm}^3/\text{mol s}$. It is observed from the plots in Figure 4.2 that the values obtained from the CBSQ method are better than the ones obtained from the G3MP2 method.

CHAPTER 5

CONCLUSION

Thermodynamic properties of the transition states are calculated in the $\text{RH} + \text{HO}_2 = \text{R}_o + \text{HOOH}$ systems using density functional calculations with enthalpies of formation (ΔH^\ddagger_{TS}) computed at the G3(MP2) level. Entropy (S°_{298}) and heat capacity ($C_p^\circ(T)$) ($300 \leq T/\text{K} \leq 1500$) contributions from vibrational, translational, and external rotation are calculated using the rigid rotor harmonic oscillator approximation based on geometric parameters and vibrational frequencies obtained at the B3LYP/6-311 G(d,p) level theory. Contributions from hindered rotors of S°_{298} and $C_p^\circ(T)$ for the transition states TCHOOH, TCCHOOH, TC_2CHOOH , TC_3CHOOH , TC_2CCHOOH and $\text{TC}_2\text{CCHOOHC}$ are calculated by the Pitzer and Gwinn approximation method while the moments of inertia are calculated from ROTATOR. The internal rotational barriers are estimated as: C-HOOH 1.0, C-CHOOH 2.8, $\text{C}_3\text{-CHOOH}$ 3.5, $\text{C}_2\text{-CCHOOH}$ 3.87 and $\text{C}_2\text{C-CHOOH}$ 3.1. Activation energies E_a , based on G3MP2//B3LYP/6-311G(d,p) calculations for HO_2 abstraction reactions are 25.81 kcal/mol for TCHOOH, 23.30 kcal/mol for TCCHOOH, 22.89 kcal/mol for TC_2CHOOH , 20.82 kcal/mol for TC_3CHOOH , 25.89 kcal/mol for TC_2CCHOOH and 24.66 kcal/mol for $\text{C}_2\text{CCHOOHC}$.

The high-pressure limit rate constants are:

$$k_{1,\infty}(\text{CH}_4 + \text{HO}_2 \rightarrow \text{TCHOOH}) = 1.22 \times 10^3 \text{ T}^{3.202} \exp(-25.81/RT) \text{ cm}^3/\text{mol-s};$$

$$k_{2,\infty}(\text{C}_2\text{H}_6 + \text{HO}_2 \rightarrow \text{TCCHOOH}) = 4.67 \times 10^2 \text{ T}^{3.355} \exp(-23.30/RT) \text{ cm}^3/\text{mol-s};$$

$$k_{3,\infty}(\text{CCC} + \text{HO}_2 \rightarrow \text{TC}_2\text{CHOOH}) = 7.14 \times 10^3 \text{ T}^{2.85} \exp(-22.89/RT) \text{ cm}^3/\text{mol-s};$$

$$k_{4,\infty}(C_3C + HO_2 \rightarrow TC_3CHOOH) = 3.18 \times 10^3 T^{3.007} \exp(-20.82/RT) \text{ cm}^3/\text{mol-s};$$

$$k_{5,\infty}(C_2CC + HO_2 \rightarrow TC_2CCHOOH) = 6.86 \times 10^3 T^{3.084} \exp(-25.89/RT) \text{ cm}^3/\text{mol-s};$$

$$k_{6,\infty}(C_2CCC + HO_2 \rightarrow TC_2CCHOOHC) = 1.72 \times 10^3 T^{2.947} \exp(-24.66/RT) \text{ cm}^3/\text{mol-s};$$

Reverse rate constants are also reported:

$$k_{-1,\infty} = 2.74 \times 10^4 T^{2.445} \exp(-9.03/RT) \text{ cm}^3/\text{mol-s}; \quad k_{-2,\infty} = 2.88 \times 10^2 T^{2.954} \exp(-10.46/RT)$$

$$\text{cm}^3/\text{mol-s}; \quad k_{-3,\infty} = 6.15 \times 10^1 T^{3.007} \exp(-12.07/RT) \text{ cm}^3/\text{mol-s}; \quad k_{-4,\infty} = 4.43 T^{3.456} \exp(-$$

$$11.9/RT) \text{ cm}^3/\text{mol-s}; \quad k_{-5,\infty} = 4.41 \times 10^2 T^{2.843} \exp(-12.63/RT) \text{ cm}^3/\text{mol-s} \text{ and } k_{-6,\infty} = 2.90 \times$$

$$10^1 T^{3.103} \exp(-13.85/RT) \text{ cm}^3/\text{mol-s}.$$

SECTION II

THERMOCHEMICAL PROPERTIES, ENTHALPY, ENTROPY AND HEAT CAPACITY (T) FOR MODEL URETHANE MONOMERS AND CORRESPONDING RADICALS

CHAPTER 1

INTRODUCTION

Polyurethanes are the single most versatile family of polymers. Polyurethane is a polymer containing the urethane linkage in its backbone chain. Polyurethanes offer a range of outstanding mechanical properties - including toughness, abrasion resistance and durability - which make them particularly suitable for demanding specialist applications such as long-lasting coatings, sophisticated adhesives and durable elastomers. However, polyurethanes' protective properties decrease over time due to sunlight-induced photodecomposition. In this work, a computational study of X-H (X = C, N) Bond Energies in two model aliphatic urethanes is undertaken. Enthalpy ($\Delta_f H^0_{(298)}$), Entropy ($\Delta S^0_{(298)}$) and Heat Capacities ($C_p(T)$, $0 \leq T/K \leq 5000$) are determined for the model urethanes - Ethyl N Ethyl carbamate, N (n-propyl) methylcarbamate and the corresponding radicals, which correspond to the loss of a H atom from the two parent molecules by using MOPAC¹ and Density Functional Calculation methods.

CHAPTER 2

CALCULATION METHOD

The geometries of the reactants and product radicals are pre-optimized using UHF/PM3 in MOPAC¹. The geometry optimization, harmonic vibration frequencies, and zero-point vibrational energies (ZPVE) are computed at the B3LYP/6-31G(d,p)²⁻⁶ level of theory using the GAUSSIAN 98^{7,11} program. The optimized geometry parameters are used to obtain total electronic energies for all species at the B3LYP/6-31G(d,p)^{12,13,14}. Total energies are corrected by ZPVE, which are scaled by 0.9806 as recommended by Scott et al.⁸ Thermal correction is taken into account using the B3LYP structure and vibrations^{9,10}.

The $\Delta H_{f(298)}^0$ are calculated using total energies and isodesmic reactions. Isodesmic reactions are hypothetical reactions where the number of electron pairs and the bonds of the same type are conserved on both sides of the equation; only the relationship among the bonds is altered. Contributions of vibration, translation, and external rotation to entropies and heat capacities are calculated from scaled vibrational frequencies and moments of inertia of the optimized structures.

The B3LYP/6-31G(d,p) method is reported to yield accurate geometries and reasonable energies when used with isodesmic working reactions¹⁵. Byrd et al. and Curtiss et al.¹⁶ both report that B3LYP/6-31G(d,p) provides accurate structures for compounds with elements up to atomic number 10.

The molecules and radicals calculated in this work are as follows: (j represents a radical site)

- CCNCO₂CC

- CCN_jCO_2CC
- CC_jNCO_2CC
- C_jCNCO_2CC
- $CCNCO_2C_jC$
- $CCNCO_2CC_j$
- $CCCNCO_2C$
- $CCCN_jCO_2C$
- CCC_jNCO_2C

The following working reactions are selected to determine $\Delta_f H^0_{(298)}$ of the target species, that are indicated in bold.

- $CCNCO_2CC + C_2NC \rightarrow C_2NCCO_2C + CCNC$
- $CCN_jCO_2CC + CH_3NH_2 \rightarrow CCNCO_2CC + CH_3N_jH$
- $CC_jNCO_2CC + CH_3NH_2 \rightarrow CCNCO_2CC + CH_{2_j}NH_2$
- $C_jCNCO_2CC + CH_3CH_2OH \rightarrow CCNCO_2CC + CH_{2_j}CH_2OH$
- $CCNCO_2C_jC + CCOC(O)C \rightarrow CCNCO_2CC + CC_jOC(O)C$
- $CCNCO_2CC_j + CCOC(O)C \rightarrow CCNCO_2CC + CCOC(O)C_j$
- $CCCNCO_2C + C_2NC \rightarrow C_2NCCO_2C + CCCN$
- $CCCN_jCO_2C + CH_3NH_2 \rightarrow CCCNCO_2C + CH_3N_jH$
- $CCC_jNCO_2C + CH_3NH_2 \rightarrow CCCNCO_2C + CH_{2_j}NH_2$

Density functional calculations with ZPVE and thermal correction are performed for all four compounds in each reaction listed above, and enthalpy of reaction ΔH^0_{rxn} is calculated from the computation values of the four compounds in a given reaction at each

level. Hess's law is used along with this calculated ΔH_{rxn}^0 and the known literature or calculated enthalpies of formation of three compounds (reference compounds) in the working reaction to estimate the enthalpy value of the target molecule or radical (in bold).

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Structures and Vibration Frequencies of Molecules and Radicals

Illustration of the fully optimized geometry at the B3LYP/6-31G(d,p) density functional calculation level for CCNCO₂CC is given in Fig 3.1. Further illustrations of the optimized geometries at the B3LYP/6-31G(d,p) level along with structural parameters like the bond lengths, angles and dihedral angles between atoms for CCCNCO₂C, CCN_jCO₂CC, CC_jNCO₂CC, C_jCNCO₂CC, CCNCO₂C_jC, CCNCO₂CC_j, CCCN_jCO₂C, CCC_jNCO₂C, C₂NCCO₂C, CH₃NH₂, CH₃N_jH, CH₂_jNH₂, CCOC(O)C, CCOC(O)C_j and CC_jOC(O)C, CCOH, C_jCOH, C₂NC, CCNC and CCCN are presented in Appendix B.1 The vibrational frequencies and moments of inertia for all the above molecules and radicals calculated at the B3LYP/6-31G(d,p) level are listed in Tables 3.1 and 3.2, respectively.

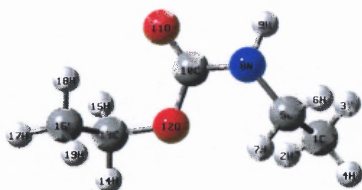


Figure 3.1 Structure of Ethyl N Ethyl Carbamate (CCNCO₂CC).

Table 3.1 Vibrational Frequencies (cm⁻¹) (calculated at B3LYP/6-31G(d,p) level)

CCNCO2CC	50.22	58.70	99.154	112.03	192.32	232.52
	278.1	342.0	403.05	435.29	494.77	570.26
	643.7	762.9	787.68	802.78	855.68	916.62
	958.8	1061.2	1097.5	1119.4	1137.7	1187.9
	1203.8	1321.3	1337.8	1355.8	1399.9	1419.6
	1424.5	1442.7	1476.4	1498.2	1500.8	1505.6
	1509.7	1520.1	1524.4	1821.3	3046.1	3052.7
	3063.9	3080.8	3111.6	3121.1	3125.9	3132.7
	3138.9	3151.9	3654.1			
CCCNCO2C	51.397	69.366	91.284	109.22	161.93	225.72
	249.47	281.04	335.05	403.52	492.86	612.39
	651.57	757.34	764.09	860.67	893.70	899.96
	1039.1	1067.7	1125.0	1139.2	1182.6	1191.4
	1214.5	1281.6	1327.9	1343.1	1378.0	1425.5
	1428.3	1475.6	1486.8	1495.1	1505.9	1509.3
	1515.3	1519.5	1523.8	1829.3	3037.8	3039.5
	3052.0	3062.3	3079.5	3106.2	3118.4	3121.5
	3139.1	3166.2	3656.7			
CCNjCO2CC	32.73	48.046	78.588	109.28	195.25	225.18
	279.22	334.94	371.45	399.94	503.60	615.31
	768.59	804.06	833.85	875.45	886.63	951.89
	1003.6	1053.9	1119.3	1131.4	1179.3	1207.3
	1278.9	1300.5	1336.7	1351.8	1408.9	1411.6
	1433.7	1498.4	1502.0	1503.1	1508.4	1521.8
	1526.7	1711.3	3033.9	3055.8	3056.0	3082.4
	3094.3	3126.7	3132.9	3134.8	3142.7	3154.5
CCjNCO2CC	45.319	70.118	101.79	143.14	177.39	216.88
	240.74	321.51	350.20	396.02	441.19	587.12
	612.08	707.18	733.17	791.22	862.22	920.95
	975.05	1019.1	1072.5	1118.3	1132.5	1201.1
	1235.1	1337.2	1377.5	1408.3	1423.0	1444.7
	1455.3	1482.8	1494.1	1500.1	1505.1	1512.3
	1523.5	1803.9	2990.5	3053.9	3076.8	3084.2
	3123.1	3125.4	3134.9	3153.9	3220.9	3637.2
CjCNCO2CC	37.673	64.694	105.18	122.64	171.13	215.73
	242.23	337.14	360.37	436.21	492.47	520.19
	555.40	675.10	760.70	788.61	836.17	869.57
	959.29	1026.8	1087.1	1110.7	1127.6	1148.0
	1200.2	1249.2	1336.9	1350.8	1387.6	1417.9
	1442.5	1468.7	1473.4	1497.5	1499.2	1504.2
	1523.6	1820.7	2990.4	3029.0	3053.2	3081.4
	3121.1	3134.1	3153.4	3167.2	3278.6	3652.5
CCNCO2Cjc	44.946	57.16	94.828	116.09	184.93	212.75
	250.29	298.19	406.98	417.66	491.72	518.72
	575.25	671.39	746.07	801.24	827.87	921.39
	958.89	1024.2	1076.3	1113.8	1141.7	1191.4
	1238.9	1317.9	1347.5	1386.8	1418.1	1426.0
	1430.5	1475.3	1478.9	1503.4	1507.9	1509.8
	1520.1	1835.8	2974.6	3047.2	3065.9	3093.3
	3113.6	3126.4	3139.5	3143.7	3203.0	3656.6

Table 3.1 Vibrational Frequencies (cm⁻¹) (continued)

CCNCO ₂ CCj	32.258	56.581	83.621	130.41	159.13	176.73
	238.20	314.26	383.09	415.41	463.09	489.81
	584.54	631.00	761.70	798.68	823.55	906.45
	957.24	1003.7	1078.3	1105.0	1130.9	1136.8
	1191.4	1240.9	1318.5	1350.2	1391.1	1422.4
	1434.6	1466.9	1477.1	1497.6	1506.3	1511.8
	1521.5	1823.8	2988.9	3046.4	3048.9	3065.0
	3111.4	3125.5	3138.9	3176.8	3287.4	3655.1
CCCNjCO ₂ C	31.076	49.432	80.367	122.32	156.50	235.12
	244.63	281.80	315.78	400.33	494.39	630.01
	764.86	780.20	871.84	889.59	920.14	1003.3
	1030.2	1078.8	1143.0	1177.6	1178.7	1219.3
	1268.8	1300.5	1313.9	1336.4	1365.1	1425.3
	1480.5	1496.1	1505.8	1510.0	1511.1	1514.4
	1528.1	1715.5	3025.8	3044.8	3051.6	3063.4
	3080.0	3096.4	3119.9	3121.2	3140.2	3175.9
CCCjNCO ₂ C	43.783	59.655	104.89	132.93	151.38	202.75
	242.35	260.29	323.26	368.30	399.84	607.86
	622.97	723.58	734.12	788.74	866.92	915.89
	1037.4	1077.0	1082.4	1139.9	1182.2	1213.8
	1236.7	1273.6	1321.4	1407.5	1424.8	1457.2
	1481.7	1492.7	1495.2	1506.5	1511.5	1516.9
	1523.1	1811.8	2970.4	3044.1	3056.9	3064.6
	3111.5	3123.3	3142.5	3170.6	3204.6	3637.0

The moments of inertia of the polyurethanes and corresponding radicals optimized at the B3LYP/6-311G(d,p) level are listed in Table 3.2 . The units are in GHz.

Table 3.2 Moments of Inertia^{a,b}

Species	Ia	Ib	Ic
CCNCO ₂ CC	3.7307403	1.1663177	1.0131828
CCCNCO ₂ C	3.8436449	1.0489492	0.8919668
CCNjCO ₂ CC	5.2949706	1.0136952	0.9552654
CCjNCO ₂ CC	3.2386413	1.3861900	1.0598035
CjCNCO ₂ CC	4.5456294	1.0487746	0.9237799
CCNCO ₂ CjC	3.4923328	1.2514025	1.0615856
CCNCO ₂ CCj	2.9496749	1.3206689	0.9983932
CCCNjCO ₂ C	4.8839553	0.9170984	0.8797683
CCCjNCO ₂ C	3.9352476	1.1262856	0.8929850

^aOptimized at the B3LYP/6-31G(d,p) level of theory. ^bUnits in GHz.

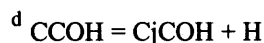
3.2 Enthalpies of Formation ($\Delta_f H^0_{(298)}$)

The $\Delta_f H^0_{(298)}$ values are calculated using the total energies and working isodesmic reactions. Enthalpies of formation $\Delta_f H^0_{(298)}$ and their respective uncertainties for reference species used in the working reactions are adopted from the literature data or are calculated using previous work; values for these reference species are listed in Table 3.3.

Table 3.3 $\Delta_f H^0_{(298)}$ for Reference Species used in Reaction Schemes and Bond Energy Calculations

Species	$\Delta_f H^0_{(298)}$ (kcal/mol)	Species	$\Delta_f H^0_{(298)}$ (kcal/mol)
C ₂ NCCO ₂ C	-88.53 ^a ± 0.19	CCOH	-56.23 ^b ± 0.12
CCOC(O)C	-106.46 ^c ± 0.20	C _j COH	-5.83 ^d ± 0.12
CC _j OC(O)C	-60.86 ^f ± 0.20	CCOC(O)C _j	-59.57 ^h ± 0.20
CH ₃ NH ₂	-5.50 ⁱ	CH ₃ N _j H	43.26 ^j
CH _{2j} NH ₂	36.26 ^j	CH ₄	-17.8 ± 0.1 ^k
CH ₃ CH ₃	-20.0 ± 0.1 ^k	CCN	-11.3 ± 0.17 ^l
CCNC	-11.29 ^m ± 0.44	C ₂ NC	-5.67 ± 0.18 ⁿ
CCCN	-16.7 ± 0.2 ^p		

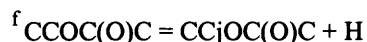
^a Reference 17 ^b Reference 18 ^c Reference 19



$$\Delta H_{\text{Rxn}} = \text{Bond Energy} = 102.5^e \text{ kcal/mol}$$

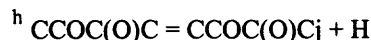
$$\text{C}_j\text{COH} = -56.23^b \pm 0.12 - 52.1 + 102.5 = -5.83 \pm 0.12 \text{ kcal/mol}$$

^e Reference 20



$$\Delta H_{\text{Rxn}} = \text{Bond Energy} = 97.7 \text{ kcal/mol}$$

$$\text{CC}_j\text{OC(O)C} = -106.46^c \pm 0.20 - 52.1 + 97.7 = -60.86 \pm 0.20 \text{ kcal/mol}$$



$$\Delta H_{\text{Rxn}} = \text{Bond Energy} = 98.99^g \text{ kcal/mol}$$

$$\text{CCOC(O)C}_j = -106.46^c \pm 0.20 - 52.1 + 98.99 = -59.57 \pm 0.20 \text{ kcal/mol}$$

ⁱ Reference 21 ^j THERM²² ^k Reference 23 ^l Reference 24

^mcalculated at the B3LYP/6-31 G(d,p) level using the isodesmic reaction: CCNC + C = CCN + CC

ⁿ Reference 25 ^pReference 26

Enthalpies of formation ($\Delta H_{f(298)}^0$) are estimated using total energies and calculated ΔH_{rxn}^0 for the listed reactions. The total energies of species are from structures optimized at the B3LYP/6-31 G(d,p) level. The ZPVE, scaled ZPVE and the thermal correction to 298.15 K are listed in Table 3.4. The total energies at 298 K from the reaction enthalpies and $\Delta H_{f(298)}^0$ of the molecules and radicals presented for B3LYP/6-31 G(d,p) calculation level are listed in Table 3.5.

Table 3.4 Total Energy^a, ZPVE, and Thermal Corrections

Species	ZPVE ^b	Sum of elec ^c	Sum of zpe ^d	Thermal Corr ^e	ZPE ^f
CCNCO ₂ CC	0.165264	-402.234151	-402.223615	6.61	101.69
C ₂ NC	0.120602	-174.365569	-174.359209	3.99	74.21
C ₂ NCCO ₂ C	0.164269	-402.19429	-402.183661	6.67	101.08
CCNC	0.121186	-174.37237	-174.365818	4.11	74.57
CCCNCO ₂ C	0.165155	-402.228878	-402.218128	6.75	101.63
CCCN	0.121594	-174.378298	-174.371714	4.13	74.82
CH ₃ NH ₂	0.064205	-95.799481	-95.795143	2.72	39.51
CH ₃ NjH	0.048905	-95.149173	-95.14479	2.75	30.09
CH ₂ jNH ₂	0.050349	-95.154985	-95.15065	2.72	30.98
CCNjCO ₂ CC	0.151082	-401.572552	-401.562001	6.62	92.97
CCjNCO ₂ CC	0.151135	-401.587572	-401.576823	6.75	93.00
CjCNCO ₂ CC	0.150096	-401.574408	-401.563585	6.79	92.36
CH ₃ CH ₂ OH	0.080164	-154.966045	-154.960823	3.28	49.33
CH ₂ jCH ₂ OH	0.064027	-154.306124	-154.301068	3.17	39.40
CCNCO ₂ CjC	0.150598	-401.579456	-401.568642	6.79	92.67
CCNCO ₂ CCj	0.149583	-401.57385	-401.562813	6.93	92.04
CCOC(O)C	0.118269	-307.588331	-307.580088	5.17	72.78
CCjOC(O)C	0.103858	-306.940711	-306.932332	5.26	63.91
CCOC(O)Cj	0.10452	-306.936434	-306.928389	5.05	64.31
CCCNjCO ₂ C	0.151021	-401.567409	-401.556692	6.73	92.93
CCCNCO ₂ C	0.165155	-402.228878	-402.218128	6.75	101.63
CCCNjNCO ₂ C	0.150971	-401.581789	-401.570808	6.89	92.90

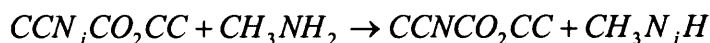
^aOptimized at the B3LYP/6-31 G(d,p) level of theory, ^bZPVE : Zero Point Correction in Hartree/Particle, ^cSum of elec = Sum of electronic and zero-point energies in kcal/mol, ^dSum of zpe = Sum of electronic and thermal enthalpies, ^eThermal Corr: Thermal Corrections in Hartree, ^fscaled zero-point energies in kcal/mol (scaled by 0.9806); Unit in Hartree = 627.51 kcal/mol

Table 3.5 Energy Values

Species	H _f B3LYP/6-31 G(d,p) ^a	Total Energy B3LYP/6-31 G(d,p) ^b
CCNCO ₂ CC	-402.3994148	-402.2268209
C ₂ NC	-174.4861714	-174.3615491
C ₂ NCCO ₂ C	-402.3585599	-402.18684872
CCNC	-174.4935563	-174.36816931
CCCNCO ₂ C	-402.3940332	-402.2213322
CCCN	-174.4998925	-174.3740734
CH ₃ NH ₂	-95.863686	-95.7963886
CH ₃ NjH	-95.1980779	-95.14573866
CH ₂ jNH ₂	-95.2053339	-95.15162667
CCNjCO ₂ CC	-401.7236339	-401.5649319
CCjNCO ₂ CC	-401.7387072	-401.5797552
CjCNCO ₂ CC	-401.7245038	-401.5664967
CH ₃ CH ₂ OH	-155.0462094	-154.9623786
CH ₂ jCH ₂ OH	-154.3701511	-154.301068
CCNCO ₂ CjC	-401.7300536	-401.5715632
CCNCO ₂ CCj	-401.7234324	-401.5657143
CCOC(O)C	-307.7066008	-307.5823832
CCjOC(O)C	-307.0445683	-306.93434615
CCOC(O)Cj	-307.0409533	-306.93041599
CCCNjCO ₂ C	-401.7184303	-401.5596221
CCCNCO ₂ C	-402.3940332	-402.2213322
CCCjNCO ₂ C	-401.7327609	-401.5737377

^aH_f in Hartree ^b B3LYP/6-31 G(d,p). Total Energies are in Hartree at 0 K

The ΔH_{rxn}^0 and $\Delta H_{\text{f}(298)}^0$ for the urethanes, Ethyl N Ethyl Carbamate (CCNCO₂CC), N (n-propyl) Methyl Carbamate (CCCNCO₂C) and the corresponding radicals calculated at the B3LYP/6-31 G(d,p) are presented in Table 3.6. The ΔH_{rxn}^0 (298) and ΔH_{f}^0 (298) for the two urethanes and the radicals are also calculated in MOPAC¹ and are presented in Table 3.7 and Table 3.8 for comparison purposes. One reaction (example), used to calculate $\Delta H_{\text{f}(298)}^0$ (CCN_jCO₂CC) is:



$$\Delta H_{\text{f}(298)}^0 = \Delta H_{\text{f}(298)}^0(\text{CCNCO}_2\text{CC}) + \Delta H_{\text{f}(298)}^0(\text{CH}_3\text{N}_j\text{H}) - (\Delta H_{\text{f}(298)}^0(\text{CCN}_j\text{CO}_2\text{CC}) + \Delta H_{\text{f}(298)}^0(\text{CH}_3\text{NH}_2))$$

Table 3.6 Reaction Enthalpies and Enthalpies of Formation

Isodesmic Reactions	ΔH_{rxn} B3LYP/ 6-31 G(d,p) kcal/mol	ΔH_{f}^0 (298) B3LYP/ 6-31G(d,p) kcal/mol
$CCNCO_2CC + C_2NC \rightarrow C_2NCCO_2C + CCNC$	20.93	-115.08
$CCCNCO_2CC + C_2NC \rightarrow C_2NCCO_2C + CCCN$	13.78	-113.34
$CCN_jCO_2CC + CH_3NH_2 \rightarrow CCNCO_2CC + CH_3N_jH$	-7.05	-59.27
$CC_jNCO_2CC + CH_3NH_2 \rightarrow CCNCO_2CC + CH_2_jNH_2$	-1.45	-71.87
$C_jCNCO_2CC + CCOH \rightarrow CCNCO_2CC + C_jCOH$	-0.16	-64.52
$CCNCO_2C_jC + CCOC(O)C \rightarrow CCNCO_2CC + CC_jOC(O)C$	-4.53	-64.95
$CCNCO_2CC_j + CCOC(O)C \rightarrow CCNCO_2CC + CCOC(O)C_j$	-5.74	-62.45
$CCCN_jCO_2C + CH_3NH_2 \rightarrow CCCNCO_2C + CH_3N_jH$	-6.94	-57.64
$CCC_jNCO_2C + CH_3NH_2 \rightarrow CCCNCO_2C + CH_2_jNH_2$	-1.78	-69.80

The reaction enthalpies and $\Delta_f H^0$ (298) are calculated at the B3LYP/6-31 G(d,p) level.

The recommended $\Delta H_{f(298)}^0$ values are -115.08 kcal/mol for CCNCO_2CC , -113.34 kcal/mol for CCCNCO_2C , -59.27 kcal/mol for $\text{CCN}_j\text{CO}_2\text{CC}$, -71.87 kcal/mol for $\text{CC}_j\text{NCO}_2\text{CC}$, -64.52 kcal/mol for $\text{C}_j\text{CNCO}_2\text{CC}$, -64.95 kcal/mol for $\text{CCNCO}_2\text{C}_j\text{C}$, -62.45 kcal/mol for $\text{CCNCO}_2\text{CC}_j$, -57.64 kcal/mol for $\text{CCCN}_j\text{CO}_2\text{C}$ and -69.80 kcal/mol for $\text{CCC}_j\text{NCO}_2\text{C}$.

Table 3.7 H_f values directly from MOPAC

Species	H_f (kcal/mol)	Species	H_f (kcal/mol)
CCNCO_2CC	-95.06	CCCNCO_2C	-99.85
$\text{CCN}_j\text{CO}_2\text{CC}$	-61.84	$\text{CC}_j\text{NCO}_2\text{CC}$	-73.31
$\text{C}_j\text{CNCO}_2\text{CC}$	-62.486	$\text{CCNCO}_2\text{C}_j\text{C}$	-66.62
$\text{CCNCO}_2\text{CC}_j$	-58.52	$\text{CCCN}_j\text{CO}_2\text{C}$	-67.82
$\text{CCC}_j\text{NCO}_2\text{C}$	-72.38	$\text{C}_2\text{NCCO}_2\text{C}$	-89.58
CCNC	-12.25	C_2NC	-10.83
CH_3NH_2	-5.18	$\text{CH}_3\text{N}_j\text{H}$	27.58
CH_2NH_2	20.77	CCOH	-56.852
C_jCOH	-20.811	$\text{CCOC}(\text{O})\text{C}$	-97.69
$\text{CC}_j\text{OC}(\text{O})\text{C}$	-70.53	$\text{CCOC}(\text{O})\text{C}$	-57.84
CCCN	-14.96		

Table 3.8 Enthalpies of Formation $\Delta H_{f(298)}^0$ from MOPAC Working Reaction

Isodesmic Reaction	ΔH_{rxn} kcal/mol	$\Delta H_{f(298)}^0$ kcal/mol
$\text{CCN}_j\text{CO}_2\text{CC} + \text{CH}_3\text{NH}_2 \rightarrow \text{CCNCO}_2\text{CC} + \text{CH}_3\text{N}_j\text{H}$	-0.46	-48.66
$\text{CC}_j\text{NCO}_2\text{CC} + \text{CH}_3\text{NH}_2 \rightarrow \text{CCNCO}_2\text{CC} + \text{CH}_2\text{NH}_2$	4.2	-60.32
$\text{C}_j\text{CNCO}_2\text{CC} + \text{CCOH} \rightarrow \text{CCNCO}_2\text{CC} + \text{C}_j\text{COH}$	3.47	-50.95
$\text{CCNCO}_2\text{C}_j\text{C} + \text{CCOC}(\text{O})\text{C} \rightarrow \text{CCNCO}_2\text{CC} + \text{CC}_j\text{OC}(\text{O})\text{C}$	-1.28	-51.0
$\text{CCNCO}_2\text{CC}_j + \text{CCOC}(\text{O})\text{C} \rightarrow \text{CCNCO}_2\text{CC} + \text{CCOC}(\text{O})\text{C}_j$	3.31	-54.3
$\text{CCCN}_j\text{CO}_2\text{C} + \text{CH}_3\text{NH}_2 \rightarrow \text{CCCNCO}_2\text{C} + \text{CH}_3\text{N}_j\text{H}$	0.73	-57.67
$\text{CCC}_j\text{NCO}_2\text{C} + \text{CH}_3\text{NH}_2 \rightarrow \text{CCCNCO}_2\text{C} + \text{CH}_2\text{NH}_2$	-1.52	-62.74

The $\Delta H_{f(298)}^0$ have been calculated using the enthalpy values obtained from MOPAC and literature.

3.3 Entropy and Heat Capacity

The S^0_{298} and $C_p(T)$ ($300 \leq T/K \leq 1500$) calculation results obtained using the geometries and harmonic frequencies at the B3LYP/6-31G(d,p) level are summarized in Table 3.9. The data represent the sum of contributions from translational, external rotation, and vibrations for S^0_{298} and $C_p(T)$'s. The symmetry number is taken into account. Contributions from internal rotors are not analyzed in this study. The SMCPs input files are included in the Appendix B.2. The scaled vibrational frequencies and moments of inertia are given in Tables 3.1 and 3.2 respectively.

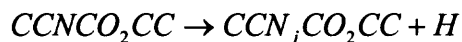
Table 3.9 Entropy and Heat Capacities of Urethanes and Radicals

Species	Symmetry	S^b_{298}	$C_p^b_{300}$	400	500	600	800	1000	1500
CCNCO ₂ CC	9	92.28	35.41	44.44	52.72	59.83	70.96	79.12	91.68
CCCNCO ₂ C	9	93.44	35.50	44.35	52.57	59.68	70.86	79.05	91.67
CCNjCO ₂ CC	9	95.05	34.58	43.16	51.03	57.76	68.22	75.84	87.43
CCjNCO ₂ CC	9	94.11	35.85	44.25	51.86	58.35	68.48	75.89	87.30
CjCNCO ₂ CC	6	95.76	36.21	44.77	52.41	58.87	68.87	76.17	87.44
CCNCO ₂ CjC	9	94.93	36.00	44.46	52.07	58.55	68.64	76.01	87.37
CCNCO ₂ CCj	6	97.56	36.51	44.99	52.58	59.00	68.97	76.24	87.47
CCCNjCO ₂ C	9	96.13	34.63	43.05	50.87	57.61	68.12	75.78	87.42
CCcjNCO ₂ C	9	95.78	35.97	44.21	51.76	58.25	68.40	75.84	87.29

Data is from B3LYP/6-31 G(d,p) level of calculation. ^bUnits in cal/(mol k).

3.4 Bond Energies

The bond energies are calculated at the B3LYP/6-31G(d,p) level and are presented in Table 3.10. The bond energies are also calculated in MOPAC and these values are compared with literature values in Table 3.11. The MOPAC data are not very accurate but are presented for reference purposes – illustration of deviations. Bond Energies are estimated using the $\Delta H_{f(298)}^0$ values of the two urethanes Ethyl N Ethyl carbamate [C-C-N-C(O)-O-C-C] and N (n-propyl) methylcarbamate [C-C-C-N-C(O)-O-C] and corresponding radicals calculated in this work. The BDE calculation is shown for the following reaction as an example.



$$-114.75 \quad -58.94 \quad 52.1(\text{kcal/mol})$$

$$\Delta H_{\text{Rxn}} = \text{Bond Energy} = -58.94 + 52.1 + 114.75 = 107.91 \text{ kcal/mol} = 453.2 \text{ kJ/mol}$$

Table 3.10 Bond Energies^a

	B. E. (kcal/mol)	B. E. (kJ/mol)
CCNCO ₂ CC → CCN _j CO ₂ CC + H	107.91	453.23
CCNCO ₂ CC → CC _j NCO ₂ CC + H	95.31	400.28
CCNCO ₂ CC → C _j CNCO ₂ CC + H	102.46	430.33
CCNCO ₂ CC → CCNCO ₂ C _j C + H	102.23	429.37
CCNCO ₂ CC → CCNCO ₂ CC _j + H	104.73	438.84
CCCNCO ₂ C → CCCN _j CO ₂ C + H	107.80	452.76
CCCNCO ₂ C → CCC _j NCO ₂ C + H	95.64	401.68

^a B.E.'s are calculated at the B3LYP/6-31 G(d,p) level of calculation.

Table 3.11 Comparison of Bond Energies Calculated from MOPAC and Gaussian with Literature Values

Species	MOPAC (Isodesmic Reaction) kJ/mol	Gaussian kJ/mol	Literature ^a kJ/mol
CH ₃ -CH ₂ -N _j -C(O)-O-CH ₂ -CH ₃	412.15	453.2	466.1
CH ₃ -C _j H-NH-C(O)-O-CH ₂ -CH ₃	363.17	400.3	402.1
C _j H ₂ -CH ₂ -NH-C(O)-O-CH ₂ -CH ₃	401.5	430.1	424.8
CH ₃ -CH ₂ -NH-C(O)-O-C _j H-CH ₃	415.7	429.4	416.9
CH ₃ -CH ₂ -NH-C(O)-O-CH ₂ -C _j H ₂	388.46	439.9	425.5
CH ₃ -CH ₂ -CH ₂ -N _j -C(O)-O-CH ₃	428.82	452.7	452.8
CH ₃ -CH ₂ -C _j H-NH-C(O)-O-CH ₃	408.87	401.7	401.7

^a[27].

CHAPTER 4

CONCLUSION

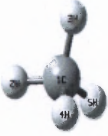
Thermodynamic properties of CCNCO₂CC, CCCNCO₂C and the corresponding radicals are calculated at the B3LYP/6-31G(d,p) density functional level and with isodesmic reaction schemes. $\Delta H_{f(298)}^0$ values calculated are -115.08 kcal/mol for CCNCO₂CC, -113.34 kcal/mol for CCCNCO₂C, -59.27 kcal/mol for CCN_jCO₂CC, -71.87 kcal/mol for CC_jNCO₂CC, -64.52 kcal/mol for C_jCNCO₂CC, -64.95 kcal/mol for CCNCO₂C_jC, -62.45 kcal/mol for CCNCO₂CC_j, -57.64 kcal/mol for CCCN_jCO₂C and -69.80 kcal/mol for CCC_jNCO₂C. S_{298}^0 and $C_p(T)$ ($300 \leq T/K \leq 1500$) values are calculated with B3LYP/6-31G(d,p) optimized geometries and frequencies. Carbon and nitrogen – hydrogen bond energies are calculated in this study as 453.2 (kJ.mol) for C-C-N_j-C(O)-O-C-C, 400.3 kJ.mol for C-C_j-N-C(O)-O-C-C, 430.1 kJ.mol for C_j-C-N-C(O)-O-C-C, 429.4 kJ.mol for C-C-N-C(O)-O-C_j-C, 439.9 kJ.mol for C-C-N-C(O)-O-C-C_j, 452.7 kJ.mol for C-C-C-N_j-C(O)-O-C, 401.7 kJ.mol for C-C-C_j-N-C(O)-O-C, where j represents the radical site are compared with those from previous studies.

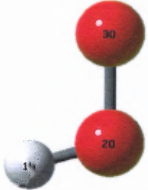
SECTION I

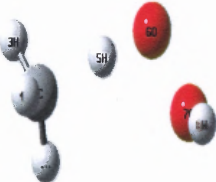
APPENDIX A

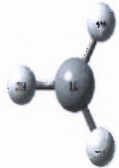
Appendix A consists of eight parts. A.1 lists the optimized geometry parameters of the compounds and the transition states in the hydrogen abstraction reactions considered in this study at the B3LYP/6-311G(d,p) density calculation level. A.2 has the illustrations of the optimized geometries of the transition states at the B3LYP/6-311G(d,p) level. A.3 contains the THERMKIN calculations for the determination of the high- pressure rate constants at the G3MP2//B3LYP/6-311G(d,p) level of calculation and A.4 contains the THERMKIN calculations at the CBSQ//B3LYP/6-311G(d,p) level of calculation. The literature values for rate constants at different temperatures are tabulated in A.5, A.6 lists the SMCPS input files for the computation of S^0_{298} and $C_p(T)$. A.7 and A.8 contain the vibir and rotator input files for the calculation of the internal rotors in the transition states at the B3LYP/6-311G(d,p) level.

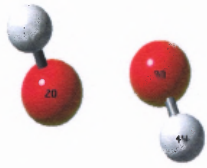
A.1 Geometry Parameters Optimized at the B3LYP/6-311G(d,p) Level

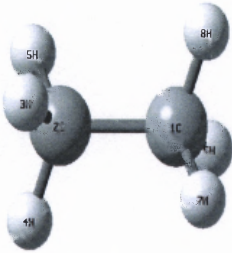
Species and structure A.1.1 CH ₄	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(2,1)	1.0907	1341.4836	1341.5612	1341.6072
	R2	R(3,1)	1.0907	1560.4361	1560.5356	3026.2387
	R3	R(4,1)	1.0908	3131.7326	3131.8447	3131.8462
	R4	R(5,1)	1.0908			
	A ^b 1	A(2,1,3)	109.4748	Moments of inertia ^c		
	A2	A(2,1,4)	109.4692			
	A3	A(3,1,4)	109.4712			
	A4	A(2,1,5)	109.4692			
	A5	A(3,1,5)	109.4712			
	A6	A(4,1,5)	109.4717			
				158.06031	158.05811	158.05293

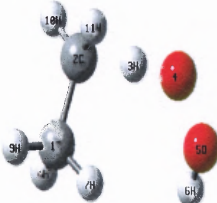
Species and Structure A.1.2 HO ₂	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(2,1)	0.9756	1162.5374	1427.5821	3604.4538
	R2	R(3,2)	1.3282			
	A ^b 1	A(1,2,3)	105.5438	Moments of inertia ^c		

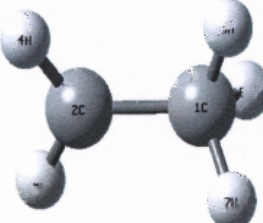
Species and Structure A.1.3 T C-HOOH	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(1,2)	1.086	-1435.3193	29.7336	155.2882
	R2	R(2,3)	1.0856	328.4010	447.8372	510.6830
	R3	R(2,4)	1.0855	604.1934	965.9512	982.5885
	R4	R(2,5)	1.441	1176.6383	1382.7102	1418.3779
	R5	R(5,6)	1.1112	1419.8004	1473.9434	3067.1314
	R6	R(6,7)	1.4151	3217.2397	3219.0984	3740.9887
	R7	R(7,8)	0.9679			
	A ^b 1	A(1,2,3)	115.7437	Moments of inertia ^c		
	A2	A(1,2,4)	115.8747			
	A3	A(1,2,5)	99.5571			
	A4	A(3,2,4)	115.7227			
	A5	A(3,2,5)	102.3474			
	A6	A(4,2,5)	104.1431			
	A7	A(5,6,7)	104.8164			
	A8	A(6,7,8)	102.1352			
	A9	L(2,5,6,3,-1)	181.3814			
	A10	L(2,5,6,3,-2)	179.503			
	D ^c 1	D(1,2,6,7)	-20.7485	30.99933	5.42806	4.84144
D2	D(3,2,6,7)	-140.0625				
D3	D(4,2,6,7)	98.9621				
D4	D(5,6,7,8)	-101.0731				

Species and Structure A.1.4 CH ₃ j	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(2,1)	1.0804	505.1162	1403.2028	1403.2949
	R2	R(3,1)	1.0805	3103.9201	3282.8597	3282.9716
	R3	R(4,1)	1.0805			
	A ^b 1	A(2,1,3)	120.0027	Moments of inertia ^e		
	A2	A(2,1,4)	120.0026			
	A3	A(3,1,4)	119.9943	286.38337	286.35565	143.18508
	D ^c 1	D(2,4,1,3)	180.2362			

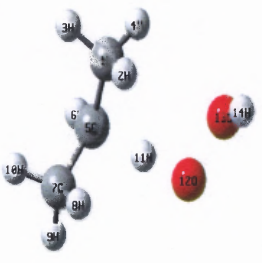
Species and Structure A.1.5 HOOH	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(2,1)	0.9659	344.4558	943.3294	1302.4117
	R2	R(3,2)	1.4536	1456.1370	3781.7053	3782.9340
	R3	R(4,3)	0.9659			
	A ^b 1	A(1,2,3)	100.0913	Moments of inertia ^e		
	A2	A(2,3,4)	100.0914			
	D ^c 1	D(4,3,2,1)	120.2408	303.04329	26.49914	25.41123

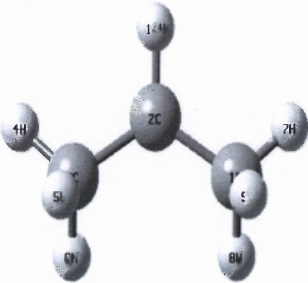
Species and Structure A.1.6 C ₂ H ₆	Name	Definition	Value	Frequencies ^d		
	R ^{a1}	R(2,1)	1.5304	305.8654	826.8498	827.5076
	R2	R(3,2)	1.0936	997.5961	1218.6842	1219.5010
	R3	R(4,2)	1.0936	1409.7483	1425.3385	1504.6720
	R4	R(5,2)	1.0936	1504.9147	1507.1829	1507.8182
	R5	R(6,1)	1.0936	3025.0210	3025.6840	3070.9292
	R6	R(7,1)	1.0936	3071.1152	3096.2724	3096.4223
	R7	R(8,1)	1.0936			
	A ^{b1}	A(1,2,3)	111.3661	Moments of inertia ^e		
	A2	A(1,2,4)	111.3786			
	A3	A(3,2,4)	107.5053	80.58815	19.91540	19.91524
	A4	A(1,2,5)	111.374			
	A5	A(3,2,5)	107.5031			
	A6	A(4,2,5)	107.5049			
	A7	A(2,1,6)	111.3663			
	A8	A(2,1,7)	111.374			
	A9	A(6,1,7)	107.503			
	A10	A(2,1,8)	111.3786			
	A11	A(6,1,8)	107.5052			
	A12	A(7,1,8)	107.5049			
	D ^{c1}	D(3,2,1,6)	179.9998			
	D2	D(3,2,1,7)	60.0053			
D3	D(3,2,1,8)	-59.9998				
D4	D(4,2,1,6)	59.9995				
D5	D(4,2,1,7)	-59.995				
D6	D(4,2,1,8)	179.9998				
D7	D(5,2,1,6)	-60.0057				
D8	D(5,2,1,7)	179.9998				
D9	D(5,2,1,8)	59.9947				

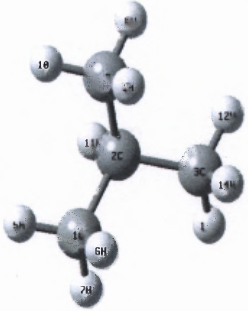
Species and Structure A.1.7 T CC-HOOH	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(1,2)	1.5022	-1602.7444	52.3031	115.3390
	R2	R(1,7)	1.0936	162.7953	262.3167	390.6833
	R3	R(1,8)	1.0932	500.6567	563.9687	828.6246
	R4	R(1,9)	1.0991	872.1334	984.3343	1028.9604
	R5	R(2,3)	1.3955	1069.8875	1196.2906	1224.3240
	R6	R(2,10)	1.0891	1378.2873	1399.9706	1460.4527
	R7	R(2,11)	1.0891	1479.8780	1489.2073	1494.9808
	R8	R(3,4)	1.1447	2989.7749	3054.9258	3081.4096
	R9	R(4,5)	1.4153	3090.5684	3165.3258	3739.9779
	R10	R(5,6)	0.9679			
	A ^b 1	A(2,1,7)	111.2068	Moments of inertia ^e 12.65842 3.52166 2.95398		
	A2	A(2,1,8)	111.6907			
	A3	A(2,1,9)	111.012			
A4	A(7,1,8)	108.4569				
A5	A(7,1,9)	107.0608				
A6	A(8,1,9)	107.2076				
A7	A(1,2,3)	105.2472				
A8	A(1,2,10)	116.7654				
A9	A(1,2,11)	116.3412				
A10	A(3,2,10)	101.7876				
A11	A(3,2,11)	100.2608				
A12	A(10,2,11)	113.29				
A13	A(3,4,5)	104.6346				
A14	A(4,5,6)	102.1823				
A15	L(2,3,4,1,-1)	175.1109				
A16	L(2,3,4,1,-2)	179.889				
D ^c 1	D(7,1,2,3)	53.594				
D2	D(7,1,2,10)	165.5953				
D3	D(7,1,2,11)	-56.3427				
D4	D(8,1,2,3)	-67.7249				
D5	D(8,1,2,10)	44.2764				
D6	D(8,1,2,11)	-177.6616				
D7	D(9,1,2,3)	172.6819				
D8	D(9,1,2,10)	-75.3168				
D9	D(9,1,2,11)	62.7452				
D10	D(1,2,4,5)	-37.7164				
D11	D(10,2,4,5)	-159.5507				
D12	D(11,2,4,5)	83.0464				
D13	D(3,4,5,6)	100.5888				

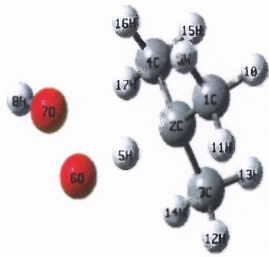
Molecule A.1.8 C ₂ H ₅	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(2,1)	1.4878	-114.2081	466.6648	815.4940
	R2	R(3,2)	1.0833	974.7314	1061.9014	1190.7044
	R3	R(4,2)	1.082	1402.1018	1466.9864	1472.4880
	R4	R(5,1)	1.092	1491.0099	2971.3512	2994.2988
	R5	R(6,1)	1.0994	3089.3278	3140.6709	3241.5555
	R6	R(7,1)	1.0998			
	A ^b 1	A(1,2,3)	120.5656	Moments of inertia ^e 103.92564 22.71349 21.04061		
	A2	A(1,2,4)	121.6996			
	A3	A(3,2,4)	117.7331			
	A4	A(2,1,5)	112.0419			
	A5	A(2,1,6)	111.8493			
	A6	A(5,1,6)	107.591			
	A7	A(2,1,7)	111.8606			
A8	A(5,1,7)	107.5208				
A9	A(6,1,7)	105.6302				
D ^c 1	D(3,2,1,5)	179.2456				
D2	D(3,2,1,6)	58.3397				
D3	D(3,2,1,7)	-59.9311				
D4	D(4,2,1,5)	-1.243				
D5	D(4,2,1,6)	-122.1489				
D6	D(4,2,1,7)	119.5803				

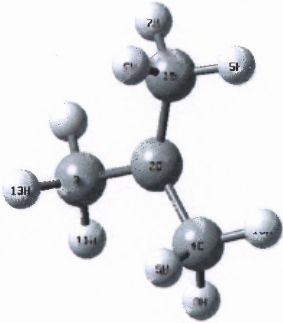
Species and Structure A.1.9 CCC	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(1,2)	1.5314	216.7043	267.0995	365.8648
	R2	R(1,7)	1.0935	754.4361	870.7429	914.1041
	R3	R(1,8)	1.0947	932.5620	1057.5944	1175.2856
	R4	R(1,9)	1.0947	1213.2486	1318.9493	1369.3024
	R5	R(2,3)	1.5314	1406.1541	1422.5712	1491.3698
	R6	R(2,10)	1.0959	1494.0210	1499.3732	1508.8395
	R7	R(2,11)	1.0959	1515.2757	3015.0328	3015.9081
	R8	R(3,4)	1.0935	3019.7383	3035.6037	3072.7540
	R9	R(3,5)	1.0947	3083.0075	3084.4974	3085.6374
	R10	R(3,6)	1.0947			
	A ^b 1	A(2,1,7)	111.5412	Moments of inertia ^e 29.53151 8.36726 7.41678		
	A2	A(2,1,8)	111.1159			
	A3	A(2,1,9)	111.1136			
	A4	A(7,1,8)	107.6957			
	A5	A(7,1,9)	107.6968			
	A6	A(8,1,9)	107.4903			
	A7	A(1,2,3)	113.0079			
	A8	A(1,2,10)	109.3845			
A9	A(1,2,11)	109.3866				
A10	A(3,2,10)	109.3849				
A11	A(3,2,11)	109.3863				
A12	A(10,2,11)	106.0534				
A13	A(2,3,4)	111.5411				
A14	A(2,3,5)	111.114				
A15	A(2,3,6)	111.1155				
A16	A(4,3,5)	107.6966				
A17	A(4,3,6)	107.6957				
A18	A(5,3,6)	107.4905				
D ^c 1	D(7,1,2,3)	-179.9312				
D2	D(7,1,2,10)	57.95				
D3	D(7,1,2,11)	-57.809				
D4	D(8,1,2,3)	59.8865				
D5	D(8,1,2,10)	-62.2323				
D6	D(8,1,2,11)	-177.9913				
D7	D(9,1,2,3)	-59.7492				
D8	D(9,1,2,10)	178.132				
D9	D(9,1,2,11)	62.373				
D10	D(1,2,3,4)	-179.9932				
D11	D(1,2,3,5)	59.8248				
D12	D(1,2,3,6)	-59.8112				
D13	D(10,2,3,4)	-57.8745				
D14	D(10,2,3,5)	-178.0566				
D15	D(10,2,3,6)	62.3074				
D16	D(11,2,3,4)	57.8845				
D17	D(11,2,3,5)	-62.2975				
D18	D(11,2,3,6)	178.0664				

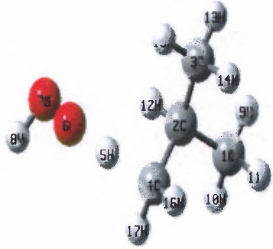
Species and Structure A.1.10 T C ₂ C-HOOH	Name	Definition	Value	Frequencies ^a		
	R ^a 1	R(1,2)	1.0946	-1656.7388	38.2478	100.9694
	R2	R(1,3)	1.0993	151.0334	188.8173	210.1366
	R3	R(1,4)	1.0929	264.0115	364.2646	413.7518
	R4	R(1,5)	1.5075	555.1450	777.0012	881.8644
	R5	R(5,6)	1.0924	932.2091	941.4965	985.5258
	R6	R(5,7)	1.5081	1102.5812	1118.6110	1188.8367
	R7	R(5,11)	1.3638	1219.2058	1356.9390	1378.9071
	R8	R(7,8)	1.0941	1397.7454	1411.5132	1476.5636
	R9	R(7,9)	1.0926	1481.9266	1488.4384	1497.9212
	R10	R(7,10)	1.0996	1500.0573	2984.2959	2988.9956
	R11	R(11,12)	1.1714	3050.6489	3055.0717	3075.2713
	R12	R(12,13)	1.4141	3092.7218	3100.5224	3738.8194
	R13	R(13,14)	0.9679			
	A ^b 1	A(2,1,3)	107.184			
	A2	A(2,1,4)	108.4816			
	A3	A(2,1,5)	111.3292			
	A4	A(3,1,4)	107.3845			
	A5	A(3,1,5)	110.9091			
	A6	A(4,1,5)	111.3679			
	A7	A(1,5,6)	113.7968			
	A8	A(1,5,7)	117.7361			
	A9	A(1,5,11)	103.877			
A10	A(6,5,7)	114.0629				
A11	A(6,5,11)	99.0364				
A12	A(7,5,11)	105.4174				
A13	A(5,7,8)	111.3928				
A14	A(5,7,9)	111.766				
A15	A(5,7,10)	110.7011				
A16	A(8,7,9)	108.2404				
A17	A(8,7,10)	107.1844				
A18	A(9,7,10)	107.3516				
A19	A(11,12,13)	104.7915				
A20	A(12,13,14)	102.2746				
A21	L(5,11,12,7,-1)	180.3348				
A22	L(5,11,12,7,-2)	185.752				
D ^c 1	D(2,1,5,6)	-174.8998				
D2	D(2,1,5,7)	47.7633				
D3	D(2,1,5,11)	-68.2954				
D4	D(3,1,5,6)	65.845				
D5	D(3,1,5,7)	-71.4919				
D6	D(3,1,5,11)	172.4494				
D7	D(4,1,5,6)	-53.6883				
D8	D(4,1,5,7)	168.9748				
D9	D(4,1,5,11)	52.9161				
D10	D(1,5,7,8)	-53.022				
D11	D(1,5,7,9)	-174.2464				
D12	D(1,5,7,10)	66.1379				
D13	D(6,5,7,8)	169.7501				
D14	D(6,5,7,9)	48.5257				
D15	D(6,5,7,10)	-71.09				
D16	D(11,5,7,8)	62.1979				
D17	D(11,5,7,9)	-59.0265				
D18	D(11,5,7,10)	-178.6422				
D19	D(1,5,12,13)	-37.4302				
D20	D(6,5,12,13)	79.9748				
D21	D(7,5,12,13)	-161.2173				
D22	D(11,12,13,14)	99.5205				
				Moments of inertia ^e		
				6.89582	2.44068	1.93365

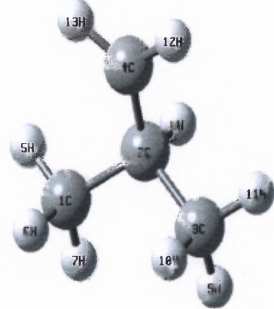
Species and Structure A.1.11 CC ₂ C	Name Definition Value	Frequencies ^d
	R ^a 1 R(1,2) 1.4904 R2 R(1,7) 1.0929 R3 R(1,8) 1.0975 R4 R(1,9) 1.1036 R5 R(2,3) 1.4904 R6 R(2,10) 1.0847 R7 R(3,4) 1.0929 R8 R(3,5) 1.1036 R9 R(3,6) 1.0975	103.4692 115.2256 352.6971 394.9236 883.1311 939.1887 944.7625 1028.0522 1146.2080 1177.6171 1367.2612 1408.1946 1412.6782 1469.5280 1477.9005 1480.2079 1491.7114 2931.7777 2936.3712 3010.9290 3012.1614 3081.8900 3082.7985 3163.0778
	A ^b 1 A(2,1,7) 112.0356 A2 A(2,1,8) 111.5715 A3 A(2,1,9) 112.0209 A4 A(7,1,8) 108.0231 A5 A(7,1,9) 106.9087 A6 A(8,1,9) 105.9489 A7 A(1,2,3) 121.087 A8 A(1,2,10) 118.8057 A9 A(3,2,10) 118.8053 A10 A(2,3,4) 112.0346 A11 A(2,3,5) 112.0233 A12 A(2,3,6) 111.569 A13 A(4,3,5) 106.9042 A14 A(4,3,6) 108.0255 A15 A(5,3,6) 105.9523 D ^c 1 D(7,1,2,3) 168.6952 D2 D(7,1,2,10) -24.4913 D3 D(8,1,2,3) 47.4341 D4 D(8,1,2,10) -145.7525 D5 D(9,1,2,3) -71.1617 D6 D(9,1,2,10) 95.6517 D7 D(1,2,3,4) -168.637 D8 D(1,2,3,5) 71.2247 D9 D(1,2,3,6) -47.3753 D10 D(10,2,3,4) 24.5495 D11 D(10,2,3,5) -95.5888 D12 D(10,2,3,6) 145.8112	Moments of inertia ^e 37.47493 8.31449 7.43320

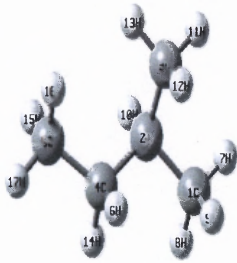
Species and Structure A.1.12 C ₃ C	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(1,2)	1.5344	213.4186	255.4930	260.7718
	R2	R(1,5)	1.0941	364.6595	368.5967	433.4416
	R3	R(1,6)	1.0957	795.6494	924.9009	925.4163
	R4	R(1,7)	1.094	958.2890	971.8596	972.9111
	R5	R(2,3)	1.5344	1190.9561	1191.4214	1209.1686
	R6	R(2,4)	1.5343	1359.5534	1360.4407	1401.9411
	R7	R(2,11)	1.0979	1402.5485	1430.0975	1484.2800
	R8	R(3,12)	1.0941	1490.4109	1491.0422	1508.8935
	R9	R(3,13)	1.0941	1509.4752	1516.4010	2995.3768
	R10	R(3,14)	1.0957	3011.1452	3011.7139	3018.9662
	R11	R(4,8)	1.094	3070.2169	3070.9244	3079.8022
	R12	R(4,9)	1.0957	3080.9312	3083.9926	3084.1579
	R13	R(4,10)	1.0941			
	A ^b 1	A(2,1,5)	111.3598	Moments of inertia ^e 7.75218 7.75089 4.48612		
	A2	A(2,1,6)	110.8263			
	A3	A(2,1,7)	111.3344			
	A4	A(5,1,6)	107.6633			
	A5	A(5,1,7)	107.8244			
	A6	A(6,1,7)	107.6607			
	A7	A(1,2,3)	111.138			
	A8	A(1,2,4)	111.1279			
	A9	A(1,2,11)	107.7419			
	A10	A(3,2,4)	111.1391			
	A11	A(3,2,11)	107.7557			
	A12	A(4,2,11)	107.7563			
	A13	A(2,3,12)	111.3534			
	A14	A(2,3,13)	111.3611			
A15	A(2,3,14)	110.8105				
A16	A(12,3,13)	107.8248				
A17	A(12,3,14)	107.6551				
A18	A(13,3,14)	107.6636				
A19	A(2,4,8)	111.3788				
A20	A(2,4,9)	110.7991				
A21	A(2,4,10)	111.3447				
A22	A(8,4,9)	107.6588				
A23	A(8,4,10)	107.8226				
A24	A(9,4,10)	107.6646				
D ^c 1	D(5,1,2,3)	-178.1296				
D2	D(5,1,2,4)	57.5432				
D3	D(5,1,2,11)	-60.2907				
D4	D(6,1,2,3)	62.0461				
D5	D(6,1,2,4)	-62.2811				
D6	D(6,1,2,11)	179.885				
D7	D(7,1,2,3)	-57.7581				
D8	D(7,1,2,4)	177.9147				
D9	D(7,1,2,11)	60.0808				
D10	D(1,2,3,12)	178.0239				
D11	D(1,2,3,13)	57.638				
D12	D(1,2,3,14)	-62.1769				
D13	D(4,2,3,12)	-57.6552				
D14	D(4,2,3,13)	-178.041				
D15	D(4,2,3,14)	62.144				
D16	D(11,2,3,12)	60.1934				
D17	D(11,2,3,13)	-60.1925				
D18	D(11,2,3,14)	179.9925				
D19	D(1,2,4,8)	-178.0958				
D20	D(1,2,4,9)	62.0913				
D21	D(1,2,4,10)	-57.7066				
D22	D(3,2,4,8)	57.5776				
D23	D(3,2,4,9)	-62.2354				
D24	D(3,2,4,10)	177.9668				
D25	D(11,2,4,8)	-60.2706				
D26	D(11,2,4,9)	179.9164				
D27	D(11,2,4,10)	60.1186				

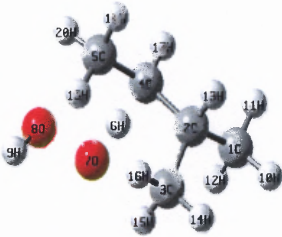
Species and Structure	Name	Definition	Value	Frequencies ^d		
A.1.13 T C₃C-HOOH 	R ^a 1	R(1,2)	1.5144	-1638.9943	33.9487	91.8919
	R2	R(1,9)	1.0928	122.8722	181.3166	206.1979
	R3	R(1,10)	1.0998	212.1653	214.7250	337.0364
	R4	R(1,11)	1.0927	368.8722	382.5514	420.7474
	R5	R(2,3)	1.5145	565.6943	793.4491	931.3556
	R6	R(2,4)	1.5143	938.0923	967.7320	988.0151
	R7	R(2,5)	1.3369	995.8323	1007.4581	1120.6019
	R8	R(3,12)	1.0931	1195.3577	1259.2269	1269.4853
	R9	R(3,13)	1.0999	1377.3899	1394.9022	1396.5849
	R10	R(3,14)	1.0933	1419.9177	1465.7928	1478.2446
	R11	R(4,15)	1.0996	1483.3741	1487.2231	1491.7978
	R12	R(4,16)	1.0935	1493.3397	1510.1080	2981.3608
	R13	R(4,17)	1.0935	2982.4994	2990.3854	3056.0731
	R14	R(5,6)	1.1971	3060.0338	3066.2675	3091.3225
	R15	R(6,7)	1.4127	3095.9288	3101.8166	3735.5623
	R16	R(7,8)	0.968			
	A ^b 1	A(2,1,9)	111.2994	Moments of inertia ^e		
	A2	A(2,1,10)	110.4524			
	A3	A(2,1,11)	111.4522	4.11953	1.86835	1.82324
	A4	A(9,1,10)	107.6581			
	A5	A(9,1,11)	108.1773			
	A6	A(10,1,11)	107.6425			
	A7	A(1,2,3)	115.2828	D ^f 1	D(9,1,2,3)	-170.2112
	A8	A(1,2,4)	114.8109	D2	D(9,1,2,4)	52.2
	A9	A(1,2,5)	102.2391	D3	D(9,1,2,5)	-58.1586
	A10	A(3,2,4)	115.2622	D4	D(10,1,2,3)	70.259
	A11	A(3,2,5)	103.9597	D5	D(10,1,2,4)	-67.3298
	A12	A(4,2,5)	102.6884	D6	D(10,1,2,5)	-177.6883
	A13	A(2,3,12)	111.5453	D7	D(11,1,2,3)	-49.3507
	A14	A(2,3,13)	110.4125	D8	D(11,1,2,4)	173.0605
	A15	A(2,3,14)	111.624	D9	D(11,1,2,5)	62.702
A16	A(12,3,13)	107.3657	D10	D(1,2,3,12)	50.8233	
A17	A(12,3,14)	108.2943	D11	D(1,2,3,13)	-68.4728	
A18	A(13,3,14)	107.4097	D12	D(1,2,3,14)	172.1248	
A19	A(2,4,15)	110.6886	D13	D(4,2,3,12)	-171.7811	
A20	A(2,4,16)	111.1424	D14	D(4,2,3,13)	68.9228	
A21	A(2,4,17)	111.56	D15	D(4,2,3,14)	-50.4796	
A22	A(15,4,16)	107.2815	D16	D(5,2,3,12)	-60.2153	
A23	A(15,4,17)	107.4389	D17	D(5,2,3,13)	-179.5114	
A24	A(16,4,17)	108.5541	D18	D(5,2,3,14)	61.0862	
A25	A(5,6,7)	104.5824	D19	D(1,2,4,15)	65.3546	
A26	A(6,7,8)	102.3879	D20	D(1,2,4,16)	-53.7564	
A27	L(2,5,6,3,-1)	182.9553	D21	D(1,2,4,17)	-175.0639	
A28	L(2,5,6,3,-2)	181.4181	D22	D(3,2,4,15)	-72.243	
			D23	D(3,2,4,16)	168.646	
			D24	D(3,2,4,17)	47.3384	
			D25	D(5,2,4,15)	175.4436	
			D26	D(5,2,4,16)	56.3327	
			D27	D(5,2,4,17)	-64.9749	
			D28	D(1,2,6,7)	68.3456	
			D29	D(3,2,6,7)	-170.9629	
			D30	D(4,2,6,7)	-50.4103	
			D31	D(5,6,7,8)	98.8041	

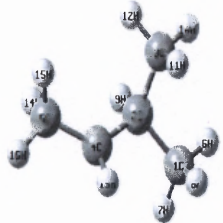
Species and Structure A.1.14 C ₃ C _j	Name Definition Value	Frequencies ^a
	R ^{a1} R(1,2) 1.4952 R2 R(1,5) 1.0949 R3 R(1,6) 1.1051 R4 R(1,7) 1.0946 R5 R(2,3) 1.4952 R6 R(2,4) 1.4952 R7 R(3,11) 1.0946 R8 R(3,12) 1.0949 R9 R(3,13) 1.1052 R10 R(4,8) 1.0947 R11 R(4,9) 1.1051 R12 R(4,10) 1.0948	129.4656 130.2361 134.7476 261.2783 379.4233 380.3539 757.2204 935.4122 936.1775 970.4860 1006.0558 1007.2579 1093.1767 1292.5659 1293.2965 1396.6085 1397.2466 1424.2066 1469.1088 1470.9600 1471.7928 1489.8591 1492.7254 1493.5284 2915.4181 2915.6906 2924.5464 3028.5825 3028.8524 3031.7821 3071.2994 3076.1501 3076.2752
	A ^{b1} A(2,1,5) 111.7545 A2 A(2,1,6) 111.9057 A3 A(2,1,7) 111.7756 A4 A(5,1,6) 106.4111 A5 A(5,1,7) 108.1963 A6 A(6,1,7) 106.4844 A7 A(1,2,3) 118.8307 A8 A(1,2,4) 118.7586 A9 A(3,2,4) 118.8363 A10 A(2,3,11) 111.7533 A11 A(2,3,12) 111.7592 A12 A(2,3,13) 111.953 A13 A(11,3,12) 108.1947 A14 A(11,3,13) 106.4739 A15 A(12,3,13) 106.392 A16 A(2,4,8) 111.7492 A17 A(2,4,9) 111.9294 A18 A(2,4,10) 111.7566 A19 A(8,4,9) 106.4641 A20 A(8,4,10) 108.2015 A21 A(9,4,10) 106.4274 D ^{c1} D(5,1,2,3) -160.1623 D2 D(5,1,2,4) 41.386 D3 D(6,1,2,3) 80.6071 D4 D(6,1,2,4) -77.8447 D5 D(7,1,2,3) -38.7317 D6 D(7,1,2,4) 162.8166 D7 D(1,2,3,11) 162.3265 D8 D(1,2,3,12) 40.9105 D9 D(1,2,3,13) -78.3313 D10 D(4,2,3,11) -39.2387 D11 D(4,2,3,12) -160.6547 D12 D(4,2,3,13) 80.1036 D13 D(1,2,4,8) -161.5275 D14 D(1,2,4,9) 79.1616 D15 D(1,2,4,10) -40.1076 D16 D(3,2,4,8) 40.022 D17 D(3,2,4,9) -79.289 D18 D(3,2,4,10) 161.4419	Moments of inertia ^c 7.98741 7.97909 4.32905

Molecule	Name	Definition	Value	Frequencies ^d		
A.1.15 C₂CC-HOOH 	R ^{a1}	R(1,2)	1.545	-1603.6678	35.3058	51.9104
	R2	R(1,9)	1.0943	101.9008	193.8203	225.5729
	R3	R(1,10)	1.0933	259.2589	328.5731	364.7802
	R4	R(1,11)	1.0944	407.1370	420.2400	543.7589
	R5	R(2,3)	1.5344	588.9662	810.1440	924.7048
	R6	R(2,4)	1.5093	927.8072	949.4566	962.4042
	R7	R(2,12)	1.0973	978.7048	1002.4587	1111.7237
	R8	R(3,13)	1.0933	1168.2914	1188.8196	1205.7043
	R9	R(3,14)	1.0955	1334.7257	1371.7475	1380.1150
	R10	R(3,15)	1.0919	1395.1578	1414.7482	1454.9533
	R11	R(4,5)	1.3946	1473.4403	1490.0074	1491.6040
	R12	R(4,16)	1.0914	1503.4359	1514.1151	3007.9049
	R13	R(4,17)	1.0906	3016.4955	3021.6365	3061.3417
	R14	R(5,6)	1.1462	3079.0844	3085.4385	3089.0208
	R15	R(6,7)	1.4162	3106.5587	3144.9070	3737.3310
	R16	R(7,8)	0.968			
	A ^{b1}	A(2,1,9)	110.3114	Moments of inertia ^e		
	A2	A(2,1,10)	111.5246			
	A3	A(2,1,11)	110.861	5.43695	1.50390	1.41560
	A4	A(9,1,10)	108.0071			
	A5	A(9,1,11)	107.9658			
	A6	A(10,1,11)	108.0433			
	A7	A(1,2,3)	111.386	D ^{f1}	D(9,1,2,3)	-57.7041
	A8	A(1,2,4)	110.2959	D2	D(9,1,2,4)	177.8487
	A9	A(1,2,12)	107.5309	D3	D(9,1,2,12)	60.7506
	A10	A(3,2,4)	111.5623	D4	D(10,1,2,3)	-177.7258
	A11	A(3,2,12)	108.2529	D5	D(10,1,2,4)	57.827
	A12	A(4,2,12)	107.6323	D6	D(10,1,2,12)	-59.271
	A13	A(2,3,13)	111.0298	D7	D(11,1,2,3)	61.8356
	A14	A(2,3,14)	110.7727	D8	D(11,1,2,4)	-62.6117
	A15	A(2,3,15)	110.746	D9	D(11,1,2,12)	-179.7097
A16	A(13,3,14)	107.7784	D10	D(1,2,3,13)	59.1042	
A17	A(13,3,15)	108.2795	D11	D(1,2,3,14)	-60.6118	
A18	A(14,3,15)	108.1172	D12	D(1,2,3,15)	179.4331	
A19	A(2,4,5)	104.6476	D13	D(4,2,3,13)	-177.1643	
A20	A(2,4,16)	116.4089	D14	D(4,2,3,14)	63.1197	
A21	A(2,4,17)	116.3702	D15	D(4,2,3,15)	-56.8354	
A22	A(5,4,16)	101.7441	D16	D(12,2,3,13)	-58.9165	
A23	A(5,4,17)	101.5968	D17	D(12,2,3,14)	-178.6325	
A24	A(16,4,17)	113.1609	D18	D(12,2,3,15)	61.4124	
A25	A(5,6,7)	104.6896	D19	D(1,2,4,5)	-171.3098	
A26	A(6,7,8)	102.2382	D20	D(1,2,4,16)	77.3019	
A27	L(4,5,6,2,-1)	176.0674	D21	D(1,2,4,17)	-60.1184	
A28	L(4,5,6,2,-2)	178.0098	D22	D(3,2,4,5)	64.3443	
			D23	D(3,2,4,16)	-47.044	
			D24	D(3,2,4,17)	175.5357	
			D25	D(12,2,4,5)	-54.2746	
			D26	D(12,2,4,16)	-165.6629	
			D27	D(12,2,4,17)	56.9167	
			D28	D(2,4,6,7)	56.1774	
			D29	D(16,4,6,7)	177.659	
			D30	D(17,4,6,7)	-64.7764	
			D31	D(5,6,7,8)	98.1803	

Molecule A.1.16 C ₃ jC	Name	Definition	Value	Frequencies ^a			
	R ^a 1	R(1,2)	1.5384	115.9010	229.4321	255.7183	
	R2	R(1,5)	1.0937	358.8655	373.8174	409.1952	
	R3	R(1,6)	1.0943	533.8048	810.6219	904.1889	
	R4	R(1,7)	1.0937	944.5650	966.0624	980.6120	
	R5	R(2,3)	1.5384	1090.8560	1178.4258	1203.6145	
	R6	R(2,4)	1.4933	1318.3471	1327.5317	1397.4805	
	R7	R(2,8)	1.106	1412.7040	1462.1983	1489.7961	
	R8	R(3,9)	1.0937	1492.9557	1503.4685	1511.7763	
	R9	R(3,10)	1.0943	2895.4676	3017.9983	3022.2562	
	R10	R(3,11)	1.0937	3082.3666	3085.7213	3086.4043	
	R11	R(4,12)	1.0841	3088.8105	3127.3745	3228.4991	
	R12	R(4,13)	1.0841				
	A ^b 1	A(2,1,5)		111.1743	Moments of inertia ^c		
	A2	A(2,1,6)		110.6713			
	A3	A(2,1,7)		111.0346			
	A4	A(5,1,6)		107.8677			
	A5	A(5,1,7)		107.8952			
	A6	A(6,1,7)		108.0638			
	A7	A(1,2,3)		111.4602			
	A8	A(1,2,4)		111.758			
	A9	A(1,2,8)		106.8143			
	A10	A(3,2,4)		111.7606			
	A11	A(3,2,8)		106.8137			
	A12	A(4,2,8)		107.915			
A13	A(2,3,9)		111.0302				
A14	A(2,3,10)		110.6716				
A15	A(2,3,11)		111.1727				
A16	A(9,3,10)		108.0642				
A17	A(9,3,11)		107.8984				
A18	A(10,3,11)		107.8699				
A19	A(2,4,12)		120.7894				
A20	A(2,4,13)		120.786				
A21	A(12,4,13)		117.7487				
D ^c 1	D(5,1,2,3)		-178.1546				
D2	D(5,1,2,4)		55.9858				
D3	D(5,1,2,8)		-61.8283				
D4	D(6,1,2,3)		61.9893				
D5	D(6,1,2,4)		-63.8703				
D6	D(6,1,2,8)		178.3157				
D7	D(7,1,2,3)		-58.0215				
D8	D(7,1,2,4)		176.1189				
D9	D(7,1,2,8)		58.3048				
D10	D(1,2,3,9)		58.0255				
D11	D(1,2,3,10)		-61.9833				
D12	D(1,2,3,11)		178.1587				
D13	D(4,2,3,9)		-176.1163				
D14	D(4,2,3,10)		63.8749				
D15	D(4,2,3,11)		-55.9831				
D16	D(8,2,3,9)		-58.3012				
D17	D(8,2,3,10)		-178.31				
D18	D(8,2,3,11)		61.832				
D19	D(1,2,4,12)		157.6215				
D20	D(1,2,4,13)		-32.012				
D21	D(3,2,4,12)		31.9271				
D22	D(3,2,4,13)		-157.7065				
D23	D(8,2,4,12)		-85.2261				
D24	D(8,2,4,13)		85.1403				

Molecule	Name	Definition	Value	Frequencies ^a		
A.1.17 C₂CCC 	R ^d 1	R(2,1)	1.535	94.4638	212.7540	223.4997
	R2	R(3,2)	1.5353	254.4034	263.1714	366.3720
	R3	R(4,2)	1.5407	413.5641	456.0860	763.7872
	R4	R(5,4)	1.5321	798.9095	912.3936	931.2353
	R5	R(6,4)	1.098	964.9641	987.1926	1024.9266
	R6	R(7,1)	1.094	1043.1989	1167.3576	1192.9927
	R7	R(8,1)	1.094	1202.8157	1297.7670	1328.2502
	R8	R(9,1)	1.0957	1370.3899	1382.7363	1402.4836
	R9	R(10,2)	1.0991	1412.9017	1421.7824	1483.9120
	R10	R(11,3)	1.0939	1490.7065	1497.9763	1501.4641
	R11	R(12,3)	1.0959	1506.3724	1509.8519	1514.8126
	R12	R(13,3)	1.0927	2982.2128	2999.5624	3012.2314
	R13	R(14,4)	1.0964	3017.8999	3021.4656	3030.8150
	R14	R(15,5)	1.0949	3070.9776	3077.1098	3080.6109
	R15	R(16,5)	1.093	3082.3458	3086.5007	3094.2830
	R16	R(17,5)	1.0935			
	A ^b 1	A(1,2,3)	110.5167	Moments of inertia ^e		
	A2	A(1,2,4)	110.5719			
	A3	A(3,2,4)	112.4827	7.26878	3.32594	2.54294
	A4	A(2,4,5)	115.0527			
	A5	A(2,4,6)	108.7553	D ^e 1	D(3,2,1,7)	-57.0994
	A6	A(5,4,6)	109.5535	D2	D(3,2,1,8)	-177.4924
	A7	A(2,1,7)	111.3206	D3	D(3,2,1,9)	62.6233
	A8	A(2,1,8)	111.4038	D4	D(4,2,1,7)	177.6915
	A9	A(7,1,8)	107.825	D5	D(4,2,1,8)	57.2985
	A10	A(2,1,9)	110.8353	D6	D(4,2,1,9)	-62.5858
	A11	A(7,1,9)	107.5986	D7	D(10,2,1,7)	60.5176
	A12	A(8,1,9)	107.6829	D8	D(10,2,1,8)	-59.8754
	A13	A(1,2,10)	107.7717	D9	D(10,2,1,9)	180.2403
	A14	A(3,2,10)	107.8462	D10	D(11,3,2,1)	55.5556
	A15	A(4,2,10)	107.4526	D11	D(11,3,2,4)	179.6747
	A16	A(2,3,11)	110.9205	D12	D(11,3,2,10)	-62.0156
	A17	A(2,3,12)	110.7154	D13	D(12,3,2,1)	-63.812
	A18	A(11,3,12)	107.5874	D14	D(12,3,2,4)	60.3071
	A19	A(2,3,13)	112.1897	D15	D(12,3,2,10)	178.6168
	A20	A(11,3,13)	107.4557	D16	D(13,3,2,1)	175.7376
A21	A(12,3,13)	107.7778	D17	D(13,3,2,4)	-60.1433	
A22	A(2,4,14)	108.3488	D18	D(13,3,2,10)	58.1664	
A23	A(5,4,14)	108.7557	D19	D(5,4,2,1)	-172.0648	
A24	A(6,4,14)	105.9858	D20	D(5,4,2,3)	63.8467	
A25	A(4,5,15)	111.0919	D21	D(5,4,2,10)	-54.6943	
A26	A(4,5,16)	112.1059	D22	D(6,4,2,1)	64.645	
A27	A(15,5,16)	107.6613	D23	D(6,4,2,3)	-59.4435	
A28	A(4,5,17)	110.914	D24	D(6,4,2,10)	-177.9846	
A29	A(15,5,17)	107.5442	D25	D(14,4,2,1)	-50.1291	
A30	A(16,5,17)	107.3121	D26	D(14,4,2,3)	-174.2176	
			D27	D(14,4,2,10)	67.2413	
			D28	D(15,5,4,2)	56.6191	
			D29	D(15,5,4,6)	179.4837	
			D30	D(15,5,4,14)	-65.0965	
			D31	D(16,5,4,2)	-63.8876	
			D32	D(16,5,4,6)	58.977	
			D33	D(16,5,4,14)	174.3968	
			D34	D(17,5,4,2)	176.1747	
			D35	D(17,5,4,6)	-60.9607	
			D36	D(17,5,4,14)	54.459	

Molecule A.1.18 T C ₂ CC-HOOH-C	Name Definition Value	Frequencies ^d
	R ^a 1 R(1,2) 1.5361 R2 R(1,10) 1.0932 R3 R(1,11) 1.0937 R4 R(1,12) 1.0941 R5 R(2,3) 1.5377 R6 R(2,4) 1.5205 R7 R(2,13) 1.1039 R8 R(3,14) 1.0931 R9 R(3,15) 1.0938 R10 R(3,16) 1.0926 R11 R(4,5) 1.5083 R12 R(4,6) 1.3675 R13 R(4,17) 1.0934 R14 R(5,18) 1.0995 R15 R(5,19) 1.0928 R16 R(5,20) 1.0927 R17 R(6,7) 1.1745 R18 R(7,8) 1.415 R19 R(8,9) 0.9679	-1660.580 25.8446 55.4226 83.1242 144.3617 159.4533 215.3732 235.4498 261.6029 274.2083 369.9556 388.3755 439.5632 463.4130 564.4991 764.1745 813.9494 914.3520 929.1653 966.8997 981.0339 1005.6415 1029.3993 1079.5111 1123.2330 1169.4306 1198.3312 1217.3191 1312.8120 1331.5351 1368.7481 1377.3780 1400.8896 1403.5286 1422.4152 1480.5321 1487.7016 1492.8585 1494.1198 1501.0031 1510.4943 1516.0770 2930.0676 2986.7845 3023.1402 3028.7353 3061.4971 3068.0506 3088.0332 3089.2105 3093.8271 3095.0684 3102.6335 3739.8332
	A ^b 1 A(2,1,10) 110.985 A2 A(2,1,11) 111.2673 A3 A(2,1,12) 110.8188 A4 A(10,1,11) 107.8954 A5 A(10,1,12) 107.9355 A6 A(11,1,12) 107.7942 A7 A(1,2,3) 110.9885 A8 A(1,2,4) 110.8837 A9 A(1,2,13) 107.6185 A10 A(3,2,4) 113.1946 A11 A(3,2,13) 107.4497 A12 A(4,2,13) 106.3834 A13 A(2,3,14) 110.4969 A14 A(2,3,15) 110.5272 A15 A(2,3,16) 112.0942 A16 A(14,3,15) 108.0884 A17 A(14,3,16) 107.4267 A18 A(15,3,16) 108.0582 A19 A(2,4,5) 119.8298 A20 A(2,4,6) 105.2583 A21 A(2,4,17) 112.7758 A22 A(5,4,6) 104.1282 A23 A(5,4,17) 112.8895 A24 A(6,4,17) 98.8802 A25 A(4,5,18) 110.75 A26 A(4,5,19) 112.3579 A27 A(4,5,20) 110.8422 A28 A(18,5,19) 107.2376 A29 A(18,5,20) 107.327 A30 A(19,5,20) 108.1154 A31 A(6,7,8) 104.8902 A32 A(7,8,9) 102.2786 A33 L(4,6,7,2,-1) 180.0946 A34 L(4,6,7,2,-2) 174.3958	Moments of inertia^c 2.96239 1.40968 1.21765 D ^e 1 D(10,1,2,3) -57.1817 D2 D(10,1,2,4) 176.1004 D3 D(10,1,2,13) 60.1291 D4 D(11,1,2,3) -177.3441 D5 D(11,1,2,4) 55.938 D6 D(11,1,2,13) -60.0333 D7 D(12,1,2,3) 62.7327 D8 D(12,1,2,4) -63.9852 D9 D(12,1,2,13) -179.9565 D10 D(1,2,3,14) 54.6457 D11 D(1,2,3,15) -64.9522 D12 D(1,2,3,16) 174.4354 D13 D(4,2,3,14) -179.9205 D14 D(4,2,3,15) 60.4815 D15 D(4,2,3,16) -60.1308 D16 D(13,2,3,14) -62.7681 D17 D(13,2,3,15) 177.6339 D18 D(13,2,3,16) 57.0216 D19 D(1,2,4,5) -178.1374 D20 D(1,2,4,6) 65.2429 D21 D(1,2,4,17) -41.4998 D22 D(3,2,4,5) 56.3725 D23 D(3,2,4,6) -60.2472 D24 D(3,2,4,17) -166.9899 D25 D(13,2,4,5) -61.4037 D26 D(13,2,4,6) -178.0235 D27 D(13,2,4,17) 75.2338 D28 D(2,4,5,18) 68.8163 D29 D(2,4,5,19) -51.0832 D30 D(2,4,5,20) -172.1699 D31 D(6,4,5,18) -173.9801 D32 D(6,4,5,19) 66.1204 D33 D(6,4,5,20) -54.9663 D34 D(17,4,5,18) -67.776 D35 D(17,4,5,19) 172.3245 D36 D(17,4,5,20) 51.2378 D37 D(2,4,7,8) 159.6562 D38 D(5,4,7,8) 33.4287 D39 D(17,4,7,8) -83.0869 D40 D(6,7,8,9) -99.3626

Molecule A.1.19 C ₂ CCjC	Name	Definition	Value	Frequencies ^d		
	R ^a 1	R(1,2)	1.5365	43.0909	103.4887	228.0471
	R2	R(1,6)	1.0939	238.6741	261.0564	334.2164
	R3	R(1,7)	1.093	347.4940	462.4364	502.1329
	R4	R(1,8)	1.0953	792.7810	901.5753	927.6973
	R5	R(2,3)	1.5491	954.8710	982.6034	1008.8748
	R6	R(2,4)	1.4989	1087.3700	1118.4777	1178.9172
	R7	R(2,9)	1.0999	1198.1276	1304.6363	1328.7825
	R8	R(3,10)	1.0949	1387.2234	1400.8566	1408.1213
	R9	R(3,11)	1.0945	1418.9330	1474.0354	1484.9244
	R10	R(3,12)	1.093	1489.0688	1491.1918	1503.2937
	R11	R(4,5)	1.491	1510.5673	2935.3542	2974.0703
	R12	R(4,13)	1.0873	3013.5588	3018.4551	3022.0251
	R13	R(5,14)	1.0964	3074.1490	3075.8437	3080.4117
	R14	R(5,15)	1.1033	3089.3850	3091.1766	3136.5855
	R15	R(5,16)	1.0936			
	A ^b 1	A(2,1,6)	111.2102	Moments of inertia ^c		
	A2	A(2,1,7)	111.1653	7.45759	3.29782	2.54929
	A3	A(2,1,8)	110.6657			
	A4	A(6,1,7)	108.1626	D ^e 1	D(6,1,2,3)	-56.5238
	A5	A(6,1,8)	107.6898	D2	D(6,1,2,4)	178.5867
	A6	A(7,1,8)	107.8015	D3	D(6,1,2,9)	60.0404
	A7	A(1,2,3)	110.5491	D4	D(7,1,2,3)	-177.1082
	A8	A(1,2,4)	111.6324	D5	D(7,1,2,4)	58.0023
	A9	A(1,2,9)	108.1312	D6	D(7,1,2,9)	-60.5441
	A10	A(3,2,4)	111.6217	D7	D(8,1,2,3)	63.1285
	A11	A(3,2,9)	106.7813	D8	D(8,1,2,4)	-61.761
	A12	A(4,2,9)	107.9047	D9	D(8,1,2,9)	179.6927
A13	A(2,3,10)	110.8014	D10	D(1,2,3,10)	57.9752	
A14	A(2,3,11)	110.6407	D11	D(1,2,3,11)	-61.8216	
A15	A(2,3,12)	111.387	D12	D(1,2,3,12)	178.1129	
A16	A(10,3,11)	108.0309	D13	D(4,2,3,10)	-177.1292	
A17	A(10,3,12)	107.9103	D14	D(4,2,3,11)	63.074	
A18	A(11,3,12)	107.9388	D15	D(4,2,3,12)	-56.9916	
A19	A(2,4,5)	122.1924	D16	D(9,2,3,10)	-59.4227	
A20	A(2,4,13)	117.8101	D17	D(9,2,3,11)	-179.2195	
A21	A(5,4,13)	118.4989	D18	D(9,2,3,12)	60.7149	
A22	A(4,5,14)	111.5493	D19	D(1,2,4,5)	-158.3365	
A23	A(4,5,15)	112.4273	D20	D(1,2,4,13)	35.8475	
A24	A(4,5,16)	111.767	D21	D(3,2,4,5)	77.3737	
A25	A(14,5,15)	106.2347	D22	D(3,2,4,13)	-88.4422	
A26	A(14,5,16)	108.0591	D23	D(9,2,4,5)	-39.6551	
A27	A(15,5,16)	106.4729	D24	D(9,2,4,13)	154.529	
			D25	D(2,4,5,14)	41.5366	
			D26	D(2,4,5,15)	-77.6834	
			D27	D(2,4,5,16)	162.639	
			D28	D(13,4,5,14)	-152.7409	
			D29	D(13,4,5,15)	88.0391	
			D30	D(13,4,5,16)	-31.6385	

^aBond Length in Å. ^bBond angle in degree. ^cDihedral angle in degree. ^dFrequencies in cm⁻¹. ^eMoments of inertia in amu.Bohr².

A.2 Illustrations of the Optimized Geometries of the Transition States

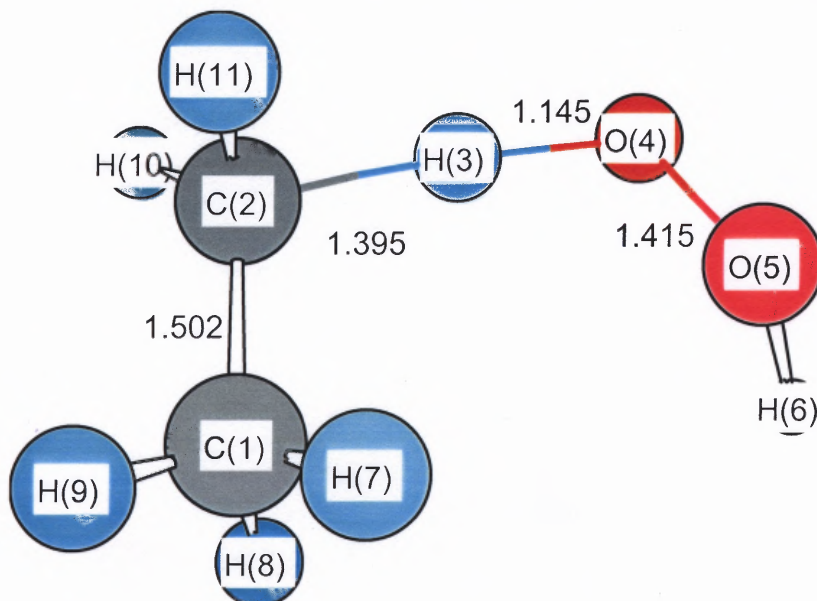


Figure A.1 Geometry of the Transition State T CC-HOOH (distances in Angstroms)

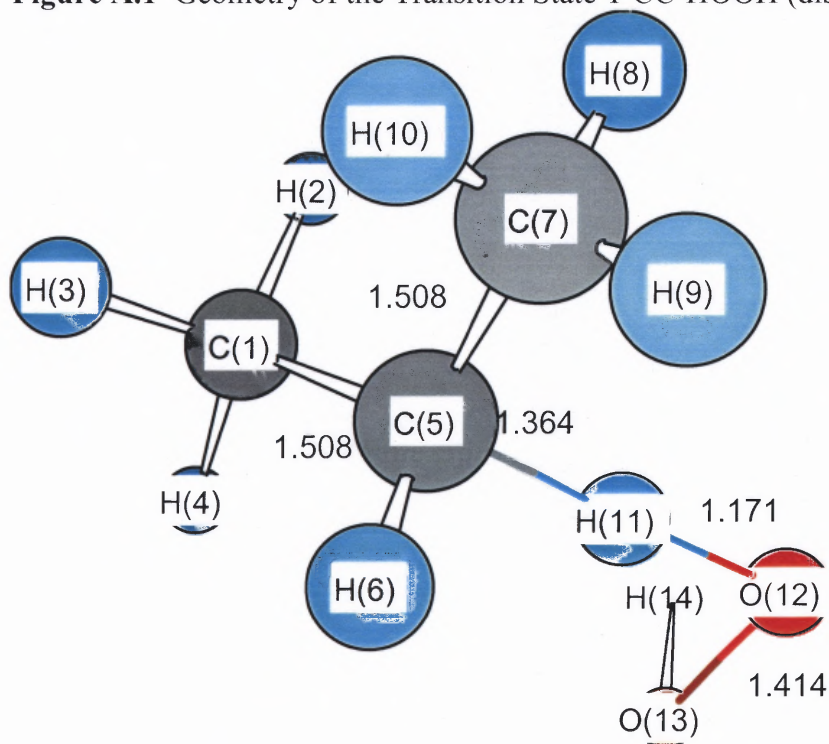


Figure A.2 Geometry of the Transition State T C₂C-HOOH (distances in Angstroms)

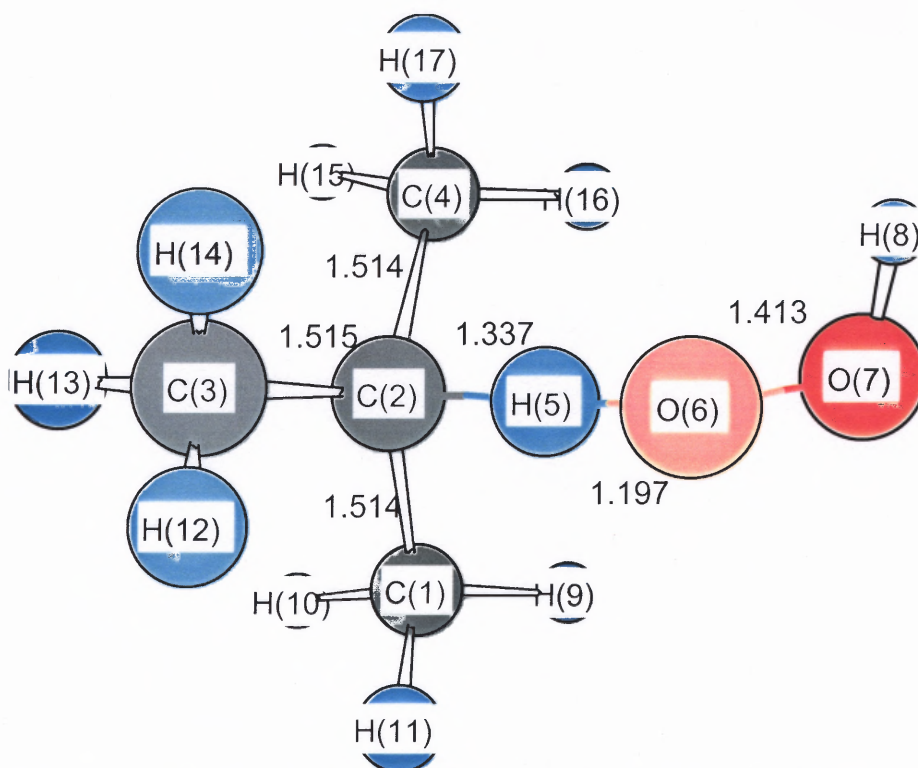


Figure A.3 Geometry of the Transition State T C₃C-HOOH (distances in Angstroms)

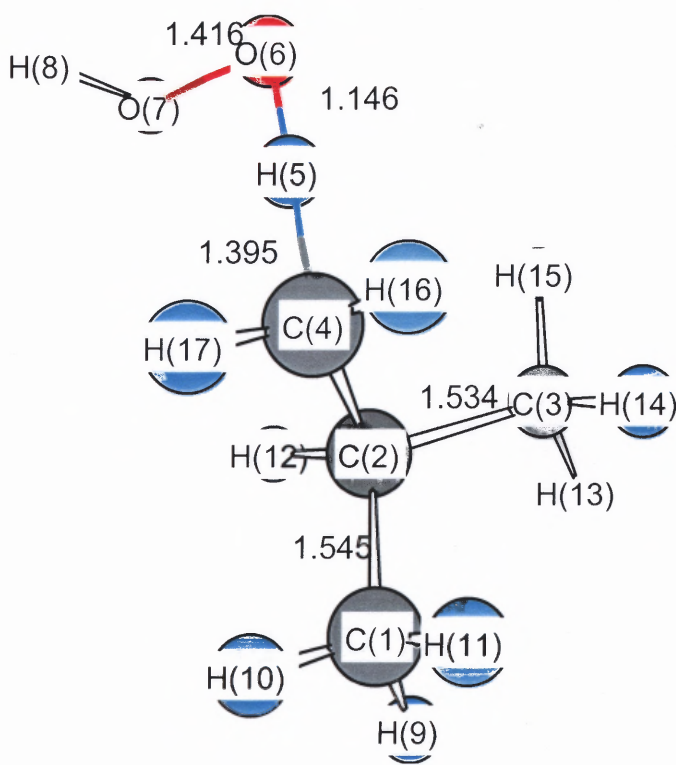


Figure A.4 Geometry of the Transition State C₂CC-HOOH (distances in Angstroms)

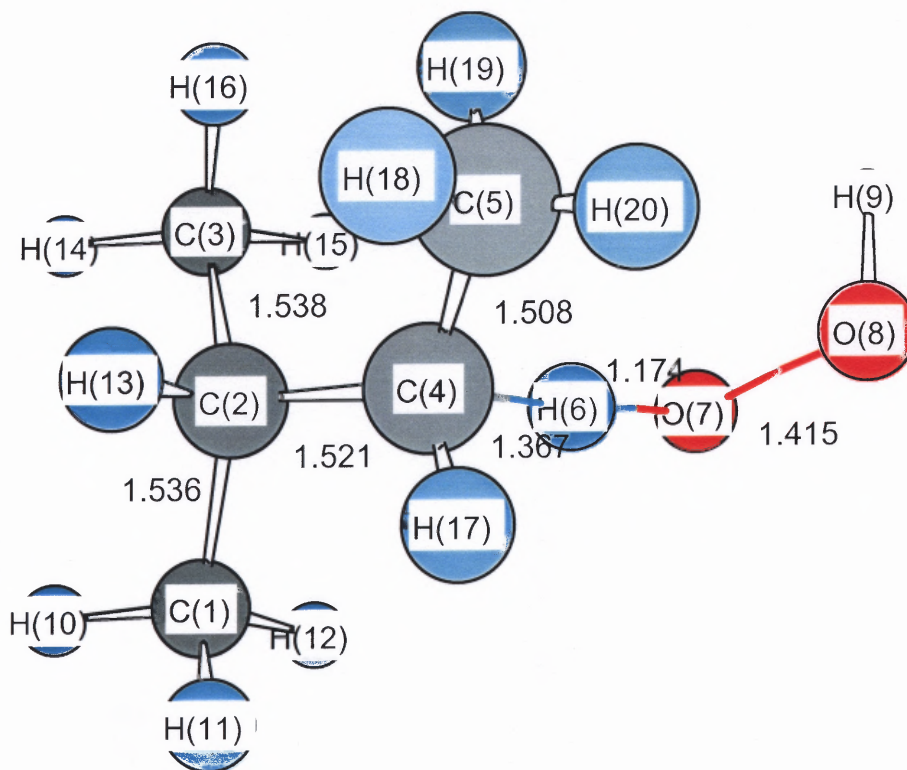
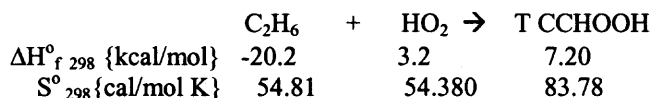


Figure A.5 Geometry of the Transition State $C_2CC-HOOHC$ (distances in Angstroms)

A.3 THERMKIN Calculations (G3MP2 Level)

Three parameters fit model equation: $k(T) = A' \times T^n \times \exp(-E_a/RT)$

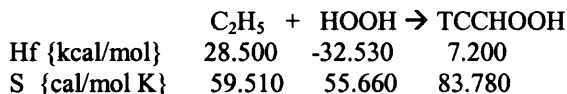
A.3.1 (a) $C_2H_6 + HO_2 \rightarrow T - CCHOOH$ (forward reaction)



Aprime = 4.6672E+02 n = 3.35546 Ea = 2.3299E+04

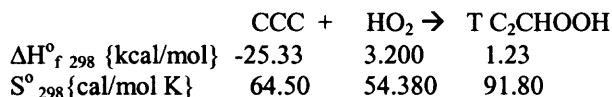
Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' ($cm^3/mol \ s$)	k_{calc} ($cm^3/mol \ s$)	k_{fit} ($cm^3/mol \ s$)
300.00	2.420E+01	-2.540E+01	9.571E+10	1.006E-06	1.014E-06
400.00	2.438E+01	-2.490E+01	2.513E+11	4.723E-02	4.667E-02
500.00	2.461E+01	-2.439E+01	5.313E+11	3.494E+01	3.471E+01
600.00	2.487E+01	-2.392E+01	9.796E+11	3.185E+03	3.189E+03
800.00	2.544E+01	-2.309E+01	2.572E+12	1.099E+06	1.108E+06
1000.00	2.603E+01	-2.243E+01	5.438E+12	4.368E+07	4.395E+07
1200.00	2.660E+01	-2.192E+01	1.003E+13	5.712E+08	5.720E+08
1500.00	2.738E+01	-2.133E+01	2.120E+13	8.568E+09	8.537E+09
2000.00	2.861E+01	-2.063E+01	5.566E+13	1.587E+11	1.582E+11

A.3.1 (b) $C_2H_5 + HOOH \rightarrow T - CCHOOH$ (reverse reaction)



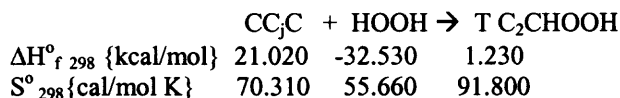
Aprime = 2.8783E+02 n = 2.95375 Ea = 1.0457E+04

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' ($cm^3/mol \ s$)	k_{calc} ($cm^3/mol \ s$)	k_{fit} ($cm^3/mol \ s$)
300.00	1.123E+01	-3.139E+01	5969431E+09	1.396E+02	1.438E+02
400.00	1.128E+01	-3.126E+01	1396274E+10	2.776E+04	2.699E+04
500.00	1.136E+01	-3.108E+01	2699098E+10	7.469E+05	7.249E+05
600.00	1.148E+01	-3.087E+01	4624878E+10	7.291E+06	7.177E+06
800.00	1.183E+01	-3.037E+01	1.08178E+11	1.483E+08	1.504E+08
1000.00	1.230E+01	-2.985E+01	2.09115E+11	1.053E+09	1.084E+09
1200.00	1.283E+01	-2.936E+01	3.58317E+11	4.343E+09	4.464E+09
1500.00	1.365E+01	-2.875E+01	6.92653E+11	2.055E+10	2.074E+10
2000.00	1.501E+01	-2.797E+01	1.62014E+12	1.208E+11	1.166E+11

A.3.2 (a) $CCC + HO_2 \rightarrow T - C_2CHOOH$ (forward reaction)

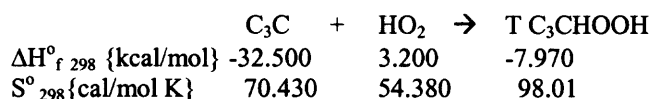
$$A_{prime} = 7.1402E+03 \quad n = 2.85325 \quad E_a = 2.2889E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	2.336E+01	-2.707E+01	8.35E+10	1.776E-06	1.759E-06
400.00	2.353E+01	-2.658E+01	1.90E+11	5.864E-02	5.899E-02
500.00	2.373E+01	-2.614E+01	3.59E+11	3.498E+01	3.538E+01
600.00	2.394E+01	-2.577E+01	6.03E+11	2.743E+03	2.769E+03
800.00	2.432E+01	-2.521E+01	1.37E+12	7.660E+05	7.644E+05
1000.00	2.464E+01	-2.485E+01	2.59E+12	2.603E+07	2.574E+07
1200.00	2.491E+01	-2.461E+01	4.36E+12	2.994E+08	2.953E+08
1500.00	2.526E+01	-2.434E+01	8.24E+12	3.833E+09	3.807E+09
2000.00	2.589E+01	-2.398E+01	1.87E+13	5.805E+10	5.901E+10

A.3.2 (b) $CC_jC + HOOH \rightarrow T - C_2CHOOH$ (reverse reaction)

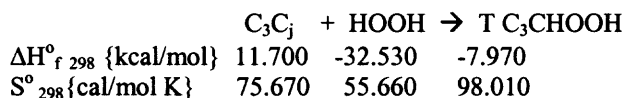
$$A_{prime} = 6.1481E+01 \quad n = 3.00686 \quad E_a = 1.2075E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	1.274E+01	-3.416E+01	1726226E+09	2.736E+00	2.752E+00
400.00	1.288E+01	-3.378E+01	4099878E+09	1.043E+03	1.034E+03
500.00	1.305E+01	-3.339E+01	8019843E+09	4.244E+04	4.224E+04
600.00	1.325E+01	-3.303E+01	1387563E+10	5.541E+05	5.541E+05
800.00	1.367E+01	-3.243E+01	3295536E+10	1.648E+07	1.655E+07
1000.00	1.409E+01	-3.196E+01	6446454E+10	1.474E+08	1.479E+08
1200.00	1.450E+01	-3.159E+01	1.11534E+11	7.031E+08	7.048E+08
1500.00	1.510E+01	-3.114E+01	2.18174E+11	3.794E+09	3.796E+09
2000.00	1.619E+01	-3.051E+01	5.18174E+11	2.493E+10	2.482E+10

A.3.3 (a) $C_3C + HO_2 \rightarrow T - C_3CHOOH$ (forward reaction)

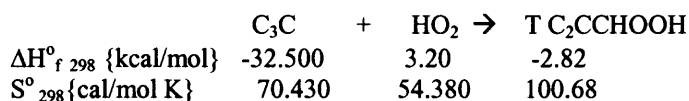
$$A_{\text{prime}} = 3.1822E+03 \quad n = 3.00697 \quad E_a = 2.0822E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' ($\text{cm}^3/\text{mol s}$)	k_{calc} ($\text{cm}^3/\text{mol s}$)	k_{fit} ($\text{cm}^3/\text{mol s}$)
300.00	2.133E+01	-2.679E+01	8.940E+10	6.161E-05	6.048E-05
400.00	2.157E+01	-2.612E+01	2.123E+11	8.790E-01	8.907E-01
500.00	2.182E+01	-2.555E+01	4.154E+11	3.219E+02	3.286E+02
600.00	2.208E+01	-2.508E+01	7.187E+11	1.840E+04	1.869E+04
800.00	2.255E+01	-2.440E+01	1.707E+12	3.513E+06	3.496E+06
1000.00	2.292E+01	-2.399E+01	3.339E+12	9.581E+07	9.391E+07
1200.00	2.320E+01	-2.373E+01	5.777E+12	9.542E+08	9.318E+08
1500.00	2.353E+01	-2.348E+01	1.130E+13	1.057E+10	1.045E+10
2000.00	2.412E+01	-2.314E+01	2.684E+13	1.383E+11	1.424E+11

A.3.3 (b) $C_3C_j + HOOH \rightarrow T - C_3CHOOH$ (reverse reaction)

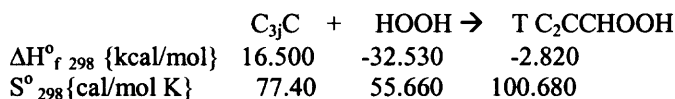
$$A_{\text{prime}} = 4.4356E+00 \quad n = 3.45615 \quad E_a = 1.1904E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' ($\text{cm}^3/\text{mol s}$)	k_{calc} ($\text{cm}^3/\text{mol s}$)	k_{fit} ($\text{cm}^3/\text{mol s}$)
300.00	1.286E+01	-3.331E+01	1615306E+09	3.431E+00	3.434E+00
400.00	1.303E+01	-3.285E+01	4365781E+09	1.379E+03	1.367E+03
500.00	1.329E+01	-3.226E+01	9440550E+09	5.888E+04	5.909E+04
600.00	1.361E+01	-3.168E+01	1772800E+10	8.081E+05	8.173E+05
800.00	1.429E+01	-3.070E+01	4791448E+10	2.660E+07	2.681E+07
1000.00	1.491E+01	-3.001E+01	1.03610E+11	2.603E+08	2.592E+08
1200.00	1.543E+01	-2.953E+01	1.94565E+11	1.337E+09	1.321E+09
1500.00	1.612E+01	-2.902E+01	4.20727E+11	7.836E+09	7.753E+09
2000.00	1.721E+01	-2.839E+01	1.13712E+12	5.615E+10	5.688E+10

A.3.4 (a) $C_3C + HO_2 \rightarrow T - C_2CCHOOH$ (forward reaction)

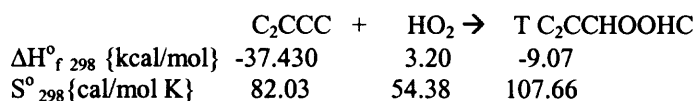
$$A_{\text{prime}} = 6.8657E+03 \quad n = 3.08366 \quad E_a = 2.5888E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' ($\text{cm}^3/\text{mol s}$)	k_{calc} ($\text{cm}^3/\text{mol s}$)	k_{fit} ($\text{cm}^3/\text{mol s}$)
300.00	2.648E+01	-2.412E+01	2.987E+11	4.179E-08	4.113E-08
400.00	2.669E+01	-2.352E+01	7.254E+11	5.138E-03	5.184E-03
500.00	2.695E+01	-2.295E+01	1.443E+12	6.829E+00	6.961E+00
600.00	2.723E+01	-2.245E+01	2.533E+12	9.237E+02	9.397E+02
800.00	2.774E+01	-2.170E+01	6.149E+12	5.209E+05	5.199E+05
1000.00	2.816E+01	-2.123E+01	1.224E+13	2.739E+07	2.687E+07
1200.00	2.846E+01	-2.095E+01	2.147E+13	4.239E+08	4.136E+08
1500.00	2.883E+01	-2.068E+01	4.272E+13	7.314E+09	7.218E+09
2000.00	2.944E+01	-2.033E+01	1.037E+14	1.493E+11	1.537E+11

A.3.4 (b) $C_3C + HOOH \rightarrow T - C_2CCHOOH$ (reverse reaction)

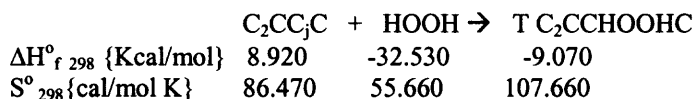
$$A_{\text{prime}} = 4.4070E+02 \quad n = 2.84324 \quad E_a = 1.2626E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' ($\text{cm}^3/\text{mol s}$)	k_{calc} ($\text{cm}^3/\text{mol s}$)	k_{fit} ($\text{cm}^3/\text{mol s}$)
300.00	1.321E+01	-3.238E+01	4866237E+09	3.061E+00	3.080E+00
400.00	1.329E+01	-3.215E+01	1102615E+10	1.405E+03	1.391E+03
500.00	1.343E+01	-3.185E+01	2079517E+10	6.316E+04	6.291E+04
600.00	1.360E+01	-3.154E+01	3492157E+10	8.764E+05	8.785E+05
800.00	1.397E+01	-3.100E+01	7912698E+10	2.793E+07	2.811E+07
1000.00	1.434E+01	-3.059E+01	1.49232E+11	2.588E+08	2.596E+08
1200.00	1.468E+01	-3.028E+01	2.50608E+11	1.258E+09	1.257E+09
1500.00	1.514E+01	-2.994E+01	4.72642E+11	6.852E+09	6.836E+09
2000.00	1.596E+01	-2.947E+01	1.07094E+12	4.472E+10	4.466E+10

A.3.5 (a) $C_2CCC + HO_2 \rightarrow T - C_2CCHOHC$ (forward reaction)

$$A_{prime} = 1.7184E+03 \quad n = 2.94685 \quad E_a = 2.4663E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	2.516E+01	-2.874E+01	3.426E+10	3.741E-08	3.682E-08
400.00	2.536E+01	-2.817E+01	7.998E+10	2.642E-03	2.669E-03
500.00	2.560E+01	-2.764E+01	1.544E+11	2.507E+00	2.555E+00
600.00	2.584E+01	-2.720E+01	2.642E+11	2.697E+02	2.739E+02
800.00	2.629E+01	-2.655E+01	6.167E+11	1.131E+05	1.127E+05
1000.00	2.664E+01	-2.616E+01	1.190E+12	4.932E+06	4.842E+06
1200.00	2.690E+01	-2.592E+01	2.037E+12	6.707E+07	6.559E+07
1500.00	2.721E+01	-2.569E+01	3.932E+12	1.013E+09	1.002E+09
2000.00	2.778E+01	-2.536E+01	9.178E+12	1.802E+10	1.851E+10

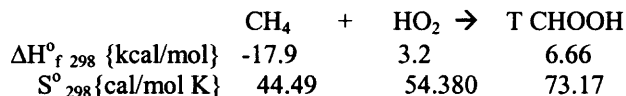
A.3.5 (b) $C_2CC_jC + HOOH \rightarrow T - C_2CCHOHC$ (reverse reaction)

$$A_{prime} = 2.9011E+01 \quad n = 3.10271 \quad E_a = 1.3847E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	1.454E+01	-3.446E+01	1.40718E+09	1.148E-01	1.148E-01
400.00	1.471E+01	-3.400E+01	3.43558E+09	9.358E+01	9.326E+01
500.00	1.492E+01	-3.353E+01	6.86568E+09	6.060E+03	6.076E+03
600.00	1.516E+01	-3.309E+01	1.20881E+10	1.086E+05	1.092E+05
800.00	1.564E+01	-3.240E+01	2.95127E+10	4.851E+06	4.862E+06
1000.00	1.608E+01	-3.190E+01	5897836E+10	5.567E+07	5.548E+07
1200.00	1.648E+01	-3.153E+01	1.03841E+11	3.139E+08	3.121E+08
1500.00	1.707E+01	-3.110E+01	2.07517E+11	1.999E+09	1.992E+09
2000.00	1.809E+01	-3.051E+01	5.06642E+11	1.545E+10	1.554E+10

A.4 Thermkin Calculation at the CBSQ Level

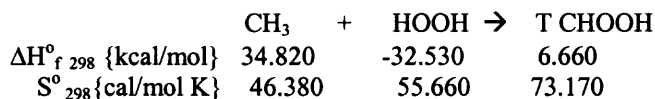
A.4.1 (a) $CH_4 + HO_2 \rightarrow T - CHOOH$ (forward reaction)



Aprime = 1.2160E+03 n = 3.20208 Ea = 2.0602E+04

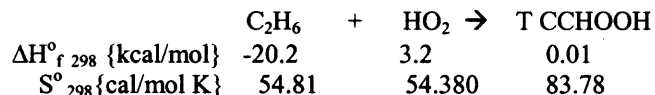
Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	kcalc (cm ³ /mol s)	kfit (cm ³ /mol s)
300.00	2.136E+01	-2.569E+01	1.040E+11	1.019E-04	1.016E-04
400.00	2.153E+01	-2.523E+01	2.612E+11	1.449E+00	1.444E+00
500.00	2.176E+01	-2.471E+01	5.336E+11	5.231E+02	5.263E+02
600.00	2.202E+01	-2.423E+01	9.567E+11	2.959E+04	2.991E+04
800.00	2.258E+01	-2.342E+01	2.403E+12	5.622E+06	5.651E+06
1000.00	2.309E+01	-2.285E+01	4.911E+12	1.552E+08	1.542E+08
1200.00	2.352E+01	-2.246E+01	8.805E+12	1.578E+09	1.557E+09
1500.00	2.405E+01	-2.206E+01	1.799E+13	1.811E+10	1.791E+10
2000.00	2.481E+01	-2.163E+01	4.519E+13	2.494E+11	2.533E+11

A.4.1 (b) $CH_3 + HOOH \rightarrow T - CHOOH$ (reverse reaction)



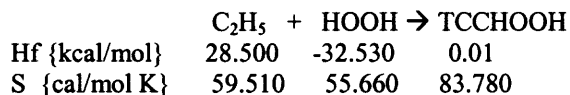
Aprime = 2.7443E+04 n = 2.44553 Ea = 3.8251E+03

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	kcalc (cm ³ /mol s)	kfit (cm ³ /mol s)
300.00	4.367E+00	-2.888E+01	3.135E+10	4.938E+07	5.122E+07
400.00	4.245E+00	-2.923E+01	6.336E+10	5.341E+08	5.149E+08
500.00	4.195E+00	-2.935E+01	1.094E+11	2.412E+09	2.327E+09
600.00	4.206E+00	-2.933E+01	1.708E+11	7.020E+09	6.903E+09
800.00	4.369E+00	-2.910E+01	3.452E+11	3.053E+10	3.111E+10
1000.00	4.659E+00	-2.878E+01	5.957E+11	8.399E+10	8.689E+10
1200.00	5.011E+00	-2.846E+01	9.304E+11	1.812E+11	1.870E+11
1500.00	5.562E+00	-2.805E+01	1.606E+12	4.405E+11	4.449E+11
2000.00	6.451E+00	-2.754E+01	3.245E+12	1.292E+12	1.239E+12

A.4.2 (a) $C_2H_6 + HO_2 \rightarrow T - CCHOOH$ (forward reaction)

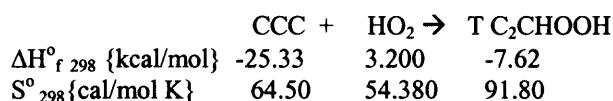
$$A_{prime} = 4.6672E+02 \quad n = 3.35546 \quad E_a = 2.3299E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' ($cm^3/mol s$)	k_{calc} ($cm^3/mol s$)	k_{fit} ($cm^3/mol s$)
300.00	1.701E+01	-2.540E+01	9.571E+10	1.741E-01	1.756E-01
400.00	1.719E+01	-2.490E+01	2.513E+11	4.008E+02	3.961E+02
500.00	1.742E+01	-2.439E+01	5.313E+11	4.857E+04	4.824E+04
600.00	1.768E+01	-2.392E+01	9.796E+11	1.325E+06	1.327E+06
800.00	1.825E+01	-2.309E+01	2.572E+12	1.013E+08	1.021E+08
1000.00	1.884E+01	-2.243E+01	5.438E+12	1.628E+09	1.639E+09
1200.00	1.941E+01	-2.192E+01	1.003E+13	1.165E+10	1.167E+10
1500.00	2.019E+01	-2.133E+01	2.120E+13	9.562E+10	9.528E+10
2000.00	2.142E+01	-2.063E+01	5.566E+13	9.689E+11	9.661E+11

A.4.2 (b) $C_2H_5 + HOOH \rightarrow T - CCHOOH$ (reverse reaction)

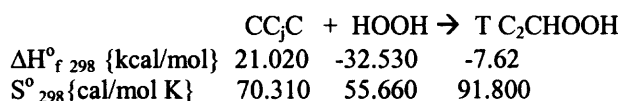
$$A_{prime} = 2.8783E+02 \quad n = 2.95375 \quad E_a = 3.2666E+03$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' ($cm^3/mol s$)	k_{calc} ($cm^3/mol s$)	k_{fit} ($cm^3/mol s$)
300.00	4.041E+00	-3.139E+01	5.969E+09	2.416E+07	2.489E+07
400.00	4.086E+00	-3.126E+01	1.396E+10	2.356E+08	2.291E+08
500.00	4.166E+00	-3.108E+01	2.699E+10	1.038E+09	1.008E+09
600.00	4.285E+00	-3.087E+01	4.625E+10	3.034E+09	2.986E+09
800.00	4.636E+00	-3.037E+01	1.082E+11	1.366E+10	1.386E+10
1000.00	5.105E+00	-2.985E+01	2.091E+11	3.927E+10	4.040E+10
1200.00	5.639E+00	-2.936E+01	3.583E+11	8.859E+10	9.105E+10
1500.00	6.456E+00	-2.875E+01	6.926E+11	2.293E+11	2.315E+11
2000.00	7.820E+00	-2.797E+01	1.620E+12	7.378E+11	7.122E+11

A.4.3 (a) $CCC + HO_2 \rightarrow T - C_2CHOOH$ (forward reaction)

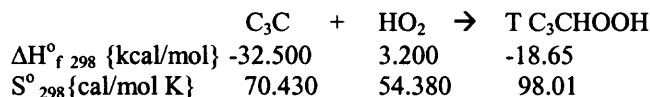
$$A_{\text{prime}} = 7.1402E+03 \quad n = 2.85325 \quad E_a = 1.4039E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	1.451E+01	-2.707E+01	8.347E+10	4.980E+00	4.932E+00
400.00	1.468E+01	-2.658E+01	1.897E+11	4.018E+03	4.042E+03
500.00	1.488E+01	-2.614E+01	3.585E+11	2.585E+05	2.615E+05
600.00	1.509E+01	-2.577E+01	6.032E+11	4.592E+06	4.636E+06
800.00	1.547E+01	-2.521E+01	1.371E+12	2.005E+08	2.001E+08
1000.00	1.579E+01	-2.485E+01	2.591E+12	2.238E+09	2.213E+09
1200.00	1.606E+01	-2.461E+01	4.359E+12	1.225E+10	1.209E+10
1500.00	1.641E+01	-2.434E+01	8.239E+12	7.466E+10	7.416E+10
2000.00	1.704E+01	-2.398E+01	1.872E+13	5.382E+11	5.471E+11

A.4.3 (b) $CC_jC + HOOH \rightarrow T - C_2CHOOH$ (reverse reaction)

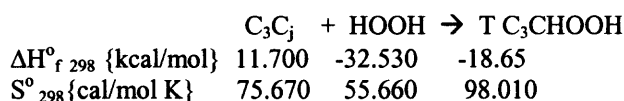
$$A_{\text{prime}} = 6.1481E+01 \quad n = 3.00686 \quad E_a = 3.2250E+03$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	3.892E+00	-3.416E+01	1.726E+09	7.671E+06	7.717E+06
400.00	4.027E+00	-3.378E+01	4.099E+09	7.145E+07	7.088E+07
500.00	4.200E+00	-3.339E+01	8.020E+09	3.136E+08	3.122E+08
600.00	4.397E+00	-3.303E+01	1.387E+10	9.278E+08	9.278E+08
800.00	4.818E+00	-3.243E+01	3.295E+10	4.315E+09	4.333E+09
1000.00	5.239E+00	-3.196E+01	6.446E+10	1.267E+10	1.272E+10
1200.00	5.646E+00	-3.159E+01	1.115E+11	2.877E+10	2.884E+10
1500.00	6.255E+00	-3.114E+01	2.182E+11	7.390E+10	7.394E+10
2000.00	7.341E+00	-3.051E+01	5.182E+11	2.312E+11	2.302E+11

A.4.4 (a) $C_3C + HO_2 \rightarrow T - C_3CHOOH$ (forward reaction)

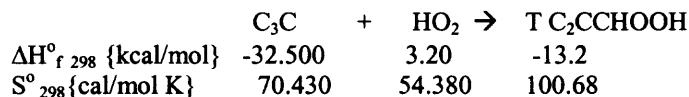
$$A_{\text{prime}} = 3.1822E+03 \quad n = 3.00697 \quad E_a = 1.0142E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	1.065E+01	-2.679E+01	8.940E+10	3.721E+03	3.653E+03
400.00	1.089E+01	-2.612E+01	2.123E+11	6.022E+05	6.103E+05
500.00	1.114E+01	-2.555E+01	4.154E+11	1.501E+07	1.532E+07
600.00	1.140E+01	-2.508E+01	7.187E+11	1.430E+08	1.453E+08
800.00	1.187E+01	-2.440E+01	1.707E+12	2.908E+09	2.894E+09
1000.00	1.224E+01	-2.399E+01	3.339E+12	2.069E+10	2.028E+10
1200.00	1.252E+01	-2.373E+01	5.777E+12	8.412E+10	8.214E+10
1500.00	1.285E+01	-2.348E+01	1.130E+13	3.806E+11	3.762E+11
2000.00	1.344E+01	-2.314E+01	2.684E+13	2.032E+12	2.092E+12

A.4.4 (b) $C_3C_j + HOOH \rightarrow T - C_3CHOOH$ (reverse reaction)

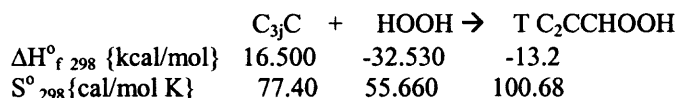
$$A_{\text{prime}} = 4.4356E+00 \quad n = 3.45615 \quad E_a = 1.2236E+03$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	2.182E+00	-3.331E+01	1.615E+09	2.072E+08	2.074E+08
400.00	2.347E+00	-3.285E+01	4.366E+09	9.451E+08	9.364E+08
500.00	2.613E+00	-3.226E+01	9.440E+09	2.745E+09	2.755E+09
600.00	2.932E+00	-3.168E+01	1.773E+10	6.280E+09	6.352E+09
800.00	3.609E+00	-3.070E+01	4.791E+10	2.202E+10	2.219E+10
1000.00	4.228E+00	-3.001E+01	1.036E+11	5.621E+10	5.597E+10
1200.00	4.755E+00	-2.953E+01	1.946E+11	1.179E+11	1.165E+11
1500.00	5.444E+00	-2.902E+01	4.207E+11	2.820E+11	2.791E+11
2000.00	6.530E+00	-2.839E+01	1.137E+12	8.251E+11	8.358E+11

A.4.5 (a) $C_3C + HO_2 \rightarrow T - C_2CCHOOH$ (forward reaction)

$$A_{\text{prime}} = 6.8657E+03 \quad n = 3.08366 \quad E_a = 1.5508E+04$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	1.610E+01	-2.412E+01	2.987E+11	1.526E+00	1.502E+00
400.00	1.631E+01	-2.352E+01	7.254E+11	2.413E+03	2.435E+03
500.00	1.657E+01	-2.295E+01	1.443E+12	2.354E+05	2.400E+05
600.00	1.685E+01	-2.245E+01	2.533E+12	5.582E+06	5.678E+06
800.00	1.736E+01	-2.170E+01	6.149E+12	3.570E+08	3.563E+08
1000.00	1.778E+01	-2.123E+01	1.224E+13	5.086E+09	4.990E+09
1200.00	1.808E+01	-2.095E+01	2.147E+13	3.295E+10	3.215E+10
1500.00	1.845E+01	-2.068E+01	4.272E+13	2.380E+11	2.349E+11
2000.00	1.906E+01	-2.033E+01	1.037E+14	2.034E+12	2.095E+12

A.4.5 (b) $C_3C + HOOH \rightarrow T - C_2CCHOOH$ (reverse reaction)

$$A_{\text{prime}} = 4.4070E+02 \quad n = 2.84324 \quad E_a = 2.2459E+03$$

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm ³ /mol s)	k_{calc} (cm ³ /mol s)	k_{fit} (cm ³ /mol s)
300.00	2.831E+00	-3.238E+01	4.866E+09	1.118E+08	1.124E+08
400.00	2.911E+00	-3.215E+01	1.103E+10	6.599E+08	6.535E+08
500.00	3.047E+00	-3.185E+01	2.079E+10	2.177E+09	2.169E+09
600.00	3.216E+00	-3.154E+01	3.492E+10	5.296E+09	5.308E+09
800.00	3.593E+00	-3.100E+01	7.913E+10	1.914E+10	1.926E+10
1000.00	3.961E+00	-3.059E+01	1.492E+11	4.804E+10	4.819E+10
1200.00	4.296E+00	-3.028E+01	2.506E+11	9.775E+10	9.771E+10
1500.00	4.761E+00	-2.994E+01	4.726E+11	2.230E+11	2.225E+11
2000.00	5.579E+00	-2.947E+01	1.071E+12	6.093E+11	6.086E+11

A.5 Literature Values of Rate Constants at Different Temperatures

A.5.1 $CH_4 + HO_2 \leftrightarrow CH_3 + HOOH$

Temp (K)	k_{lit}^6 (fwd)	k_{lit}^6 (rev)
300	5.27E-03	3.29E+10
400	1.28E+01	2.56E+10
500	1.37E+03	2.20E+10
600	3.09E+04	1.99E+10
800	1.52E+06	1.76E+10
1000	1.57E+07	1.63E+10
1200	7.48E+07	1.55E+10
1500	3.55E+08	1.48E+10
2000	1.69E+09	1.41E+10

A.5.2 $C_2H_6 + HO_2 \leftrightarrow C_2H_5 + HOOH$

Temp (K)	k_{lit}^6 (fwd)	k_{lit}^6 (rev)	$k_{densiov}^1$
300	3.83	1.70E+09	5.85E+02
400	2.02E+03	2.56E+09	3.71E+05
500	8.67E+04	3.28E+09	1.88E+07
600	1.06E+06	3.86E+09	2.65E+08
800	2.44E+07	4.73E+09	7.71E+09
1000	1.60E+08	5.35E+09	6.12E+10
1200	5.60E+08	5.80E+09	2.52E+11
1500	1.96E+09	6.30E+09	1.08E+12
2000	6.87E+09	6.83E+09	4.95E+12

A.5.3 $CCC + HO_2 \leftrightarrow CCjC + HOOH$

Temp (K)	k_{lit}^7 (fwd)	k_{lit}^7 (rev)	$k_{densiov}^1$
300	1.95E+00	3.29E+06	2.96E-01
400	1.41E+03	4.07E+07	7.05E+02
500	8.33E+04	2.12E+08	7.87E+04
600	1.38E+06	7.01E+08	1.89E+06
800	5.39E+07	3.70E+09	1.06E+08
1000	5.57E+08	1.16E+10	1.25E+09
1200	2.86E+09	2.73E+10	6.73E+09
1500	1.64E+10	7.21E+10	3.76E+10
2000	1.11E+11	2.29E+11	2.24E+11

A.5.4 $C_3C + HO_2 \leftrightarrow C_3C_j + HOOH$

Temp (K)	k_{lit}^8 (fwd)	k_{lit}^8 (rev)	$k_{densiov}^1$
300	1.59E+02	3.93E+07	9.72E+00
400	2.74E+04	1.31E+08	9.66E+03
500	6.86E+05	3.27E+08	6.39E+05
600	6.39E+06	6.82E+08	1.08E+07
800	1.21E+08	2.15E+09	3.93E+08
1000	8.05E+08	5.18E+09	3.57E+09
1200	3.10E+09	1.06E+10	1.61E+10
1500	1.32E+10	2.52E+10	7.55E+10
2000	6.67E+10	7.66E+10	3.78E+11

A.5.5 $C_3C + HO_2 \leftrightarrow C_{3j}C + HOOH$

Temp (K)	k_{lit}^8 (fwd)	k_{lit}^8 (rev)
300	3.19E-01	3.76E+07
400	4.42E+02	2.35E+08
500	3.86E+04	7.83E+08
600	8.27E+05	1.88E+09
800	4.44E+07	6.37E+09
1000	5.51E+08	1.48E+10
1200	3.22E+09	2.77E+10
1500	2.09E+10	5.69E+10
2000	1.60E+11	1.34E+11

A.6 SMCPS Input files for the Transition States in the HO₂ Abstraction

A.6.1 T-CHOOH

NAME (name of molecule)

T C-HOOH

COMMENTS:

from Tc-hooh.log in e: b3lyp/6-311g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

2 number of internal rotors

MOLECULAR WT

49

OPTICAL ISOMER

2

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

11.87

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 1 H 5 O 2 N 0

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

30.99933 5.42806 4.84144

SYMMETRY

3

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

18

-1435.3193	29.7336	155.2882
328.4010	447.8372	510.6830
604.1934	965.9512	982.5885
1176.6383	1382.7102	1418.3779
1419.8004	1473.9434	3067.1314
3217.2397	3219.0984	3740.9887

A.6.2 T-CCHOOH

NAME (name of molecule)

T CCHOOH

COMMENTS:

from Tcc-hooh.log in e: b3lyp/6-311g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

63

OPTICAL ISOMER

2

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

7.2

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 2 H 7 O 2 N 0

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

12.65842 3.52166 2.95398

SYMMETRY

3

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-
1)-1602.7444 52.3031 162.7953

24

115.3390	262.3167	390.6833
500.6567	563.9687	828.6246
872.1334	984.3343	1028.9604
1069.8875	1196.2906	1224.3240
1378.2873	1399.9706	1460.4527
1479.8780	1489.2073	1494.9808
2989.7749	3054.9258	3081.4096
3090.5684	3165.3258	3739.9779

A.6.3 T-C₂C-HOOH

NAME (name of molecule)

T C2C-HOOH

COMMENTS:

from Tc2c-hooh.log in e: b3lyp/6-311g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

77

OPTICAL ISOMER

2

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

1.23

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 3 H 9 O 2 N 0

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

6.89582 2.44068 1.93365

SYMMETRY

9

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-
1)-1656.7388 38.2478 188.8173 210.1366

32

100.9694	151.0334	
264.0115	364.2646	413.7518
555.1450	777.0012	881.8644
932.2091	941.4965	985.5258
1102.5812	1118.6110	1188.8367
1219.2058	1356.9390	1378.9071
1397.7454	1411.5132	1476.5636
1481.9266	1488.4384	1497.9212
1500.0573	2984.2959	2988.9956
3050.6489	3055.0717	3075.2713
3092.7218	3100.5224	3738.8194

A.6.4 T-C₃C-HOOH

NAME (name of molecule)
TC3c-hooh

COMMENTS:
from Tc3c-hooh.log in e: b3lyp/6-311g(d,p)

TEMPERATURE
8 (Number of temperature to be read in)
298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR
0 number of internal rotors

MOLECULAR WT
91

OPTICAL ISOMER
2

MULTIPLICITY
2 multiplicity of molecular specie of interest

HF298
-7.97

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 4 H 11 O 2 N 0
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)
1 (integer input)

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

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²
2 choice of moment of inertia units
4.11953 1.86835 1.82324

SYMMETRY
27

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-
1)-1638.9943 33.9487 181.3166 206.1979 212.1653

40

91.8919	122.8722	
214.7250	337.0364	
368.8722	382.5514	420.7474
565.6943	793.4491	931.3556
938.0923	967.7320	988.0151
995.8323	1007.4581	1120.6019
1195.3577	1259.2269	1269.4853
1377.3899	1394.9022	1396.5849
1419.9177	1465.7928	1478.2446
1483.3741	1487.2231	1491.7978
1493.3397	1510.1080	2981.3608
2982.4994	2990.3854	3056.0731
3060.0338	3066.2675	3091.3225
3095.9288	3101.8166	3735.5623

A.6.5 T-C₂CC-HOOH

NAME (name of molecule)

T C2cc-hooh

COMMENTS:

from Tc2cc-hooh.log in e: b3lyp/6-311g(d,p) c2ch-ch2-h-q sym=9

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

91

OPTICAL ISOMER

2

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

-2.82

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 4 H 11 O 2 N 0

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

5.43695 1.50390 1.41560

SYMMETRY

9

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)
-1603.6678 35.3058 51.9104 225.5729 259.2589
40

101.9008	193.8203	
328.5731	364.7802	
407.1370	420.2400	543.7589
588.9662	810.1440	924.7048
927.8072	949.4566	962.4042
978.7048	1002.4587	1111.7237
1168.2914	1188.8196	1205.7043
1334.7257	1371.7475	1380.1150
1395.1578	1414.7482	1454.9533
1473.4403	1490.0074	1491.6040
1503.4359	1514.1151	3007.9049
3016.4955	3021.6365	3061.3417
3079.0844	3085.4385	3089.0208
3106.5587	3144.9070	3737.3310

A.6.6 T C₂CC-HOOHC

NAME (name of molecule)

T C2cc-hooh-c

COMMENTS:

from Tc2cc-hoohc.log in e: b3lyp/6-311g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

105

OPTICAL ISOMER

2

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

-9.07

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 5 H 13 O 2 N 0

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

2.96239 1.40968 1.21765

SYMMETRY

27

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-
1)-1660.5800 25.8446 55.4226 159.4533 215.3732 235.4498
48

83.1242	144.3617	261.6029
274.2083	369.9556	388.3755
439.5632	463.4130	564.4991
764.1745	813.9494	914.3520
929.1653	966.8997	981.0339
1005.6415	1029.3993	1079.5111
1123.2330	1169.4306	1198.3312
1217.3191	1312.8120	1331.5351
1368.7481	1377.3780	1400.8896
1403.5286	1422.4152	1480.5321
1487.7016	1492.8585	1494.1198
1501.0031	1510.4943	1516.0770
2930.0676	2986.7845	3023.1402
3028.7353	3061.4971	3068.0506
3088.0332	3089.2105	3093.8271
3095.0684	3102.6335	3739.8332

A.7 VIBIR Input file for the transition states

```
Tc-hooh
0
0
0
1
1 c-hooh
3.406 34.31 1.0 3
```

```
Tcc-hooh
0
0
0
2
1 c-chooh
3.15 270.17 2.8 3
1 cc-hooh
39.36 38.36 1.0 3
```

```
Tc2c-hooh
0
0
0
3
1 c-cchooh
3.15 303.28 2.8 3
1 cc-chooh
3.15 235.47 2.8 3
1 ccc-hooh
76.15 35.52 1.0 3
```

```
Tc3c-hooh
0
0
0
4
1 c3-chooh
3.16 338.98 3.5 3
1 c3-chooh
3.15 263.94 3.5 3
1 c3-chooh
3.16 337.71 3.5 3
1 c3c-hooh
114.79 37.18 1.0 3
```

Tc2cc-hooh

0

0

0

4

1 c2-cchooh

3.16 144.32 3.87 3

1 c2-cchooh

3.16 445.80 3.87 3

1 c2c-chooh

274.8 73.98 3.1 3

1 c2cc-hooh

178.2 37.43 1.0 3

Tc2cc-hoohc

0

0

0

5

1 c2-cchoohc

3.15 596.17 3.87 3

1 c2-cchoohc

3.15 667.11 3.87 3

1 c2c-choohc

72.78 237.8 3.1 3

1 c2cchooh-c

3.15 421.04 2.8 3

1 c2cc-hoohc

274.2 35.33 1.0 3

A.8 ROTATOR Input Files

A.8.1 TC-HOOH

c-hooh

8

1	1	-1.644240	-1.133861	-0.470043
2	6	-1.811860	-0.171994	0.005446
3	1	-2.339784	0.564111	-0.592813
4	1	-2.078895	-0.203564	1.057144
5	1	-0.463411	0.335972	-0.000340
6	8	0.583058	0.709541	0.014440
7	8	1.383177	-0.450172	-0.117123
8	1	1.667618	-0.605650	0.794839

2 5

2 3

1 3 4

5 3

6 7 8

$V(x)=A+B*\cos(nx)+C*\sin(nx)$ b3lyp/6-3lg*

0 0 1

1

100

3

0.5

0. 0.

0. 0.

0.5 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

A.8.2 TCCHOOH

c-chooh

11

1	6	-1.645553	-0.675738	-0.111883
2	6	-1.218660	0.736596	0.170166
3	1	0.159865	0.753472	-0.046216
4	8	1.283861	0.672876	-0.247654
5	8	1.647929	-0.597085	0.259885
6	1	1.689179	-1.134245	-0.544236
7	1	-1.059386	-1.390388	0.472606
8	1	-1.540217	-0.925838	-1.170888
9	1	-2.700574	-0.829307	0.155091
10	1	-1.562416	1.501062	-0.525288
11	1	-1.255493	1.053769	1.211386

1 2

1 3

7 8 9

2 6

3 4 5 6 10 11

$$V(x)=A+B*\cos(nx)+C*\sin(nx) \quad \text{b3lyp/6-3lg*}$$

0 0 1

1

100

3

1.4

0. 0.

0. 0.

1.4 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

cc-hooh
11

1	6	-1.645553	-0.675738	-0.111883
2	6	-1.218660	0.736596	0.170166
3	1	0.159865	0.753472	-0.046216
4	8	1.283861	0.672876	-0.247654
5	8	1.647929	-0.597085	0.259885
6	1	1.689179	-1.134245	-0.544236
7	1	-1.059386	-1.390388	0.472606
8	1	-1.540217	-0.925838	-1.170888
9	1	-2.700574	-0.829307	0.155091
10	1	-1.562416	1.501062	-0.525288
11	1	-1.255493	1.053769	1.211386

2 3
2 6
1 7 8 9 10 11
3 3
4 5 6

$V(x)=A+B*\cos(nx)+C*\sin(nx)$ b3lyp/6-31g*

0 0 1
1
100
3
0.5
0. 0.
0. 0.
0.5 0.

8
298.15 300. 400. 500. 600. 800. 1000. 1500.

A.8.3 TC₂CHOOH

c-cchooh

14

1	6	-0.827443	1.442236	0.129857
2	1	-0.766135	1.417029	1.222449
3	1	-1.718615	2.030205	-0.131944
4	1	0.043035	1.980345	-0.253651
5	6	-0.911659	0.051915	-0.446830
6	1	-0.885777	0.025262	-1.538561
7	6	-1.902508	-0.904272	0.168304
8	1	-1.768839	-0.975136	1.251934
9	1	-1.812533	-1.908061	-0.253749
10	1	-2.932897	-0.564547	-0.010394
11	1	0.316137	-0.483522	-0.190325
12	8	1.375964	-0.897321	0.088657
13	8	2.250489	0.199380	-0.090916
14	1	2.363669	0.522682	0.814330

1 5

1 3

2 3 4

5 9

6 7 8 9 10 11 12 13 14

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad b31yp/6-31g^*$$

0 0 1

1

100

3

1.4

0. 0.

0. 0.

1.4 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

cc-chooh

14

1	6	-0.827443	1.442236	0.129857
2	1	-0.766135	1.417029	1.222449
3	1	-1.718615	2.030205	-0.131944
4	1	0.043035	1.980345	-0.253651
5	6	-0.911659	0.051915	-0.446830
6	1	-0.885777	0.025262	-1.538561
7	6	-1.902508	-0.904272	0.168304
8	1	-1.768839	-0.975136	1.251934
9	1	-1.812533	-1.908061	-0.253749
10	1	-2.932897	-0.564547	-0.010394
11	1	0.316137	-0.483522	-0.190325
12	8	1.375964	-0.897321	0.088657
13	8	2.250489	0.199380	-0.090916
14	1	2.363669	0.522682	0.814330

7 5

7 3

8 9 10

5 9

1 2 3 4 6 11 12 13 14

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad b3lyp/6-31g^*$$

0 0 1

1

100

3

1.4

0. 0.

0. 0.

1.4 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c2c-hooh
14

1	6	-0.827443	1.442236	0.129857
2	1	-0.766135	1.417029	1.222449
3	1	-1.718615	2.030205	-0.131944
4	1	0.043035	1.980345	-0.253651
5	6	-0.911659	0.051915	-0.446830
6	1	-0.885777	0.025262	-1.538561
7	6	-1.902508	-0.904272	0.168304
8	1	-1.768839	-0.975136	1.251934
9	1	-1.812533	-1.908061	-0.253749
10	1	-2.932897	-0.564547	-0.010394
11	1	0.316137	-0.483522	-0.190325
12	8	1.375964	-0.897321	0.088657
13	8	2.250489	0.199380	-0.090916
14	1	2.363669	0.522682	0.814330

5 11
5 9
1 2 3 4 6 7 8 9 10
11 3
12 13 14

$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx)$ b31yp/6-31g*

0 0 1
1
100
3
0.5
0. 0.
0. 0.
0.5 0.

8
298.15 300. 400. 500. 600. 800. 1000. 1500.

A.8.4 TC₃CHOOH

c3-chooh

17

1	6	0.896431	0.477172	1.445850
2	6	0.775380	0.042114	0.000393
3	6	1.686565	-1.095477	-0.411182
4	6	0.666039	1.175898	-0.997420
5	1	-0.447817	-0.496544	-0.031974
6	8	-1.567489	-0.919132	-0.060624
7	8	-2.382603	0.220956	0.116911
8	1	-2.644750	0.432200	-0.790708
9	1	0.100367	1.174449	1.718529
10	1	1.857221	0.984983	1.615183
11	1	0.849008	-0.377041	2.125601
12	1	1.610484	-1.940319	0.278305
13	1	2.735819	-0.765596	-0.411663
14	1	1.455479	-1.452571	-1.418310
15	1	1.592602	1.767757	-1.016006
16	1	-0.148639	1.856035	-0.733887
17	1	0.494478	0.803812	-2.011212

1 2

1 3

9 10 11

2 12

3 4 5 6 7 8 12 13 14 15 16 17

V(x)=A+B*COS(nx)+C*SIN(nx) b3l yp/6-3lg*

0 0 1

1

100

3

1.75

0. 0.

0. 0.

1.75 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c3-chooh

17

1	6	0.896431	0.477172	1.445850
2	6	0.775380	0.042114	0.000393
3	6	1.686565	-1.095477	-0.411182
4	6	0.666039	1.175898	-0.997420
5	1	-0.447817	-0.496544	-0.031974
6	8	-1.567489	-0.919132	-0.060624
7	8	-2.382603	0.220956	0.116911
8	1	-2.644750	0.432200	-0.790708
9	1	0.100367	1.174449	1.718529
10	1	1.857221	0.984983	1.615183
11	1	0.849008	-0.377041	2.125601
12	1	1.610484	-1.940319	0.278305
13	1	2.735819	-0.765596	-0.411663
14	1	1.455479	-1.452571	-1.418310
15	1	1.592602	1.767757	-1.016006
16	1	-0.148639	1.856035	-0.733887
17	1	0.494478	0.803812	-2.011212

3 2

3 3

12 13 14

2 12

1 4 5 6 7 8 9 10 11 15 16 17

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad b31yp/6-31g^*$$

0 0 1

1

100

3

1.75

0. 0.

0. 0.

1.75 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c3-chooh

17

1	6	0.896431	0.477172	1.445850
2	6	0.775380	0.042114	0.000393
3	6	1.686565	-1.095477	-0.411182
4	6	0.666039	1.175898	-0.997420
5	1	-0.447817	-0.496544	-0.031974
6	8	-1.567489	-0.919132	-0.060624
7	8	-2.382603	0.220956	0.116911
8	1	-2.644750	0.432200	-0.790708
9	1	0.100367	1.174449	1.718529
10	1	1.857221	0.984983	1.615183
11	1	0.849008	-0.377041	2.125601
12	1	1.610484	-1.940319	0.278305
13	1	2.735819	-0.765596	-0.411663
14	1	1.455479	-1.452571	-1.418310
15	1	1.592602	1.767757	-1.016006
16	1	-0.148639	1.856035	-0.733887
17	1	0.494478	0.803812	-2.011212

4 2

4 3

15 16 17

2 12

1 3 5 6 7 8 9 10 11 12 13 14

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad b3lyp/6-3lg^*$$

0 0 1

1

100

3

1.75

0. 0.

0. 0.

1.75 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c3c-hooh

17

1	6	0.896431	0.477172	1.445850
2	6	0.775380	0.042114	0.000393
3	6	1.686565	-1.095477	-0.411182
4	6	0.666039	1.175898	-0.997420
5	1	-0.447817	-0.496544	-0.031974
6	8	-1.567489	-0.919132	-0.060624
7	8	-2.382603	0.220956	0.116911
8	1	-2.644750	0.432200	-0.790708
9	1	0.100367	1.174449	1.718529
10	1	1.857221	0.984983	1.615183
11	1	0.849008	-0.377041	2.125601
12	1	1.610484	-1.940319	0.278305
13	1	2.735819	-0.765596	-0.411663
14	1	1.455479	-1.452571	-1.418310
15	1	1.592602	1.767757	-1.016006
16	1	-0.148639	1.856035	-0.733887
17	1	0.494478	0.803812	-2.011212

2 5

2 12

1 3 4 9 10 11 12 13 14 15 16 17

5 3

6 7 8

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad \text{b3lyp/6-31g*}$$

0 0 1

1

100

3

0.5

0. 0.

0. 0.

0.5 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

A.8.5 TC₂CCHOOH

c2-cchooh

17

1	6	2.404215	-0.637449	-0.398750
2	6	0.992851	-0.030834	-0.234008
3	6	1.062639	1.461159	0.117589
4	6	0.206256	-0.806789	0.794130
5	1	-1.089577	-0.299328	0.703413
6	8	-2.134677	0.146818	0.553785
7	8	-2.420592	-0.060319	-0.817681
8	1	-2.965191	-0.860319	-0.795210
9	1	2.961352	-0.098823	-1.171331
10	1	2.356864	-1.690603	-0.688436
11	1	2.969733	-0.567998	0.535586
12	1	0.474681	-0.133411	-1.195771
13	1	1.590987	2.022628	-0.657608
14	1	1.595534	1.613125	1.062633
15	1	0.060217	1.881295	0.221683
16	1	0.448804	-0.610965	1.840101
17	1	0.042977	-1.864110	0.582340

1 2

1 3

9 10 11

2 12

3 4 5 6 7 8 12 13 14 15 16 17

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad b31yp/6-31g^*$$

0 0 1

1

100

3

1.94

0. 0.

0. 0.

1.94 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c2-cchooh

17

1	6	2.404215	-0.637449	-0.398750
2	6	0.992851	-0.030834	-0.234008
3	6	1.062639	1.461159	0.117589
4	6	0.206256	-0.806789	0.794130
5	1	-1.089577	-0.299328	0.703413
6	8	-2.134677	0.146818	0.553785
7	8	-2.420592	-0.060319	-0.817681
8	1	-2.965191	-0.860319	-0.795210
9	1	2.961352	-0.098823	-1.171331
10	1	2.356864	-1.690603	-0.688436
11	1	2.969733	-0.567998	0.535586
12	1	0.474681	-0.133411	-1.195771
13	1	1.590987	2.022628	-0.657608
14	1	1.595534	1.613125	1.062633
15	1	0.060217	1.881295	0.221683
16	1	0.448804	-0.610965	1.840101
17	1	0.042977	-1.864110	0.582340

3 2

3 3

13 14 15

2 12

1 4 5 6 7 8 9 10 11 12 16 17

$$V(x)=A+B*\cos(nx)+C*\sin(nx) \quad b31yp/6-31g*$$

0 0 1

1

100

3

1.94

0. 0.

0. 0.

1.94 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c2c-chooh

17

1	6	2.404215	-0.637449	-0.398750
2	6	0.992851	-0.030834	-0.234008
3	6	1.062639	1.461159	0.117589
4	6	0.206256	-0.806789	0.794130
5	1	-1.089577	-0.299328	0.703413
6	8	-2.134677	0.146818	0.553785
7	8	-2.420592	-0.060319	-0.817681
8	1	-2.965191	-0.860319	-0.795210
9	1	2.961352	-0.098823	-1.171331
10	1	2.356864	-1.690603	-0.688436
11	1	2.969733	-0.567998	0.535586
12	1	0.474681	-0.133411	-1.195771
13	1	1.590987	2.022628	-0.657608
14	1	1.595534	1.613125	1.062633
15	1	0.060217	1.881295	0.221683
16	1	0.448804	-0.610965	1.840101
17	1	0.042977	-1.864110	0.582340

2 4

2 9

1 3 9 10 11 12 13 14 15

4 6

5 6 7 8 16 17

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad \text{b3lyp/6-31g*}$$

0 0 1

1

100

3

1.55

0. 0.

0. 0.

1.55 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c2cc-hooh

17

1	6	2.404215	-0.637449	-0.398750
2	6	0.992851	-0.030834	-0.234008
3	6	1.062639	1.461159	0.117589
4	6	0.206256	-0.806789	0.794130
5	1	-1.089577	-0.299328	0.703413
6	8	-2.134677	0.146818	0.553785
7	8	-2.420592	-0.060319	-0.817681
8	1	-2.965191	-0.860319	-0.795210
9	1	2.961352	-0.098823	-1.171331
10	1	2.356864	-1.690603	-0.688436
11	1	2.969733	-0.567998	0.535586
12	1	0.474681	-0.133411	-1.195771
13	1	1.590987	2.022628	-0.657608
14	1	1.595534	1.613125	1.062633
15	1	0.060217	1.881295	0.221683
16	1	0.448804	-0.610965	1.840101
17	1	0.042977	-1.864110	0.582340

4 5

4 12

1 2 3 9 10 11 12 13 14 15 16 17

5 3

6 7 8

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad b31yp/6-31g^*$$

0 0 1

1

100

3

0.5

0. 0.

0. 0.

0.5 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

A.8.6 TC₂CCHOHC

c2-cchoohc

20

1	6	1.947585	-1.149017	-0.725393
2	6	1.474738	0.183069	-0.124106
3	6	1.488552	0.129449	1.412573
4	6	0.125737	0.587909	-0.697114
5	6	-0.508455	1.889714	-0.275206
6	1	-0.751191	-0.366971	-0.262215
7	8	-1.519938	-1.143642	0.168234
8	8	-2.780718	-0.512709	0.047143
9	1	-2.928717	-0.175078	0.942039
10	1	2.947532	-1.407374	-0.366877
11	1	1.984200	-1.100561	-1.817390
12	1	1.270091	-1.962501	-0.449349
13	1	2.191638	0.962986	-0.434578
14	1	2.476724	-0.163821	1.776469
15	1	0.761497	-0.601816	1.777394
16	1	1.249128	1.097165	1.859711
17	1	0.051563	0.407735	-1.772975
18	1	0.059913	2.745165	-0.667770
19	1	-0.549364	1.999269	0.811329
20	1	-1.526712	1.969871	-0.663332

1 2

1 3

10 11 12

2 15

3 4 5 6 7 8 9 13 14 15 16 17 18 19 20

V(x)=A+B*COS(nx)+C*SIN(nx) b3lyp/6-3lg*

0 0 1

1

100

3

1.94

0. 0.

0. 0.

1.94 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c2-cchoohc

20

1	6	1.947585	-1.149017	-0.725393
2	6	1.474738	0.183069	-0.124106
3	6	1.488552	0.129449	1.412573
4	6	0.125737	0.587909	-0.697114
5	6	-0.508455	1.889714	-0.275206
6	1	-0.751191	-0.366971	-0.262215
7	8	-1.519938	-1.143642	0.168234
8	8	-2.780718	-0.512709	0.047143
9	1	-2.928717	-0.175078	0.942039
10	1	2.947532	-1.407374	-0.366877
11	1	1.984200	-1.100561	-1.817390
12	1	1.270091	-1.962501	-0.449349
13	1	2.191638	0.962986	-0.434578
14	1	2.476724	-0.163821	1.776469
15	1	0.761497	-0.601816	1.777394
16	1	1.249128	1.097165	1.859711
17	1	0.051563	0.407735	-1.772975
18	1	0.059913	2.745165	-0.667770
19	1	-0.549364	1.999269	0.811329
20	1	-1.526712	1.969871	-0.663332

3 2

3 3

14 15 16

2 15

1 4 5 6 7 8 9 10 11 12 13 17 18 19 20

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad b3lyp/6-31g^*$$

0 0 1

1

100

3

1.94

0. 0.

0. 0.

1.94 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c2c-choohc

20

1	6	1.947585	-1.149017	-0.725393
2	6	1.474738	0.183069	-0.124106
3	6	1.488552	0.129449	1.412573
4	6	0.125737	0.587909	-0.697114
5	6	-0.508455	1.889714	-0.275206
6	1	-0.751191	-0.366971	-0.262215
7	8	-1.519938	-1.143642	0.168234
8	8	-2.780718	-0.512709	0.047143
9	1	-2.928717	-0.175078	0.942039
10	1	2.947532	-1.407374	-0.366877
11	1	1.984200	-1.100561	-1.817390
12	1	1.270091	-1.962501	-0.449349
13	1	2.191638	0.962986	-0.434578
14	1	2.476724	-0.163821	1.776469
15	1	0.761497	-0.601816	1.777394
16	1	1.249128	1.097165	1.859711
17	1	0.051563	0.407735	-1.772975
18	1	0.059913	2.745165	-0.667770
19	1	-0.549364	1.999269	0.811329
20	1	-1.526712	1.969871	-0.663332

2 4

2 9

1 3 10 11 12 13 14 15 16

4 9

5 6 7 8 9 17 18 19 20

V(x)=A+B*COS(nx)+C*SIN(nx) b3lyp/6-3lg*

0 0 1

1

100

3

1.55

0. 0.

0. 0.

1.55 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c2cchooh-c

20

1	6	1.947585	-1.149017	-0.725393
2	6	1.474738	0.183069	-0.124106
3	6	1.488552	0.129449	1.412573
4	6	0.125737	0.587909	-0.697114
5	6	-0.508455	1.889714	-0.275206
6	1	-0.751191	-0.366971	-0.262215
7	8	-1.519938	-1.143642	0.168234
8	8	-2.780718	-0.512709	0.047143
9	1	-2.928717	-0.175078	0.942039
10	1	2.947532	-1.407374	-0.366877
11	1	1.984200	-1.100561	-1.817390
12	1	1.270091	-1.962501	-0.449349
13	1	2.191638	0.962986	-0.434578
14	1	2.476724	-0.163821	1.776469
15	1	0.761497	-0.601816	1.777394
16	1	1.249128	1.097165	1.859711
17	1	0.051563	0.407735	-1.772975
18	1	0.059913	2.745165	-0.667770
19	1	-0.549364	1.999269	0.811329
20	1	-1.526712	1.969871	-0.663332

5 4

5 3

18 19 20

4 15

1 2 3 6 7 8 9 10 11 12 13 14 15 16 17

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad b3lyp/6-3lg^*$$

0 0 1

1

100

3

1.4

0. 0.

0. 0.

1.4 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

c2cc-hoohc

20

1	6	1.947585	-1.149017	-0.725393
2	6	1.474738	0.183069	-0.124106
3	6	1.488552	0.129449	1.412573
4	6	0.125737	0.587909	-0.697114
5	6	-0.508455	1.889714	-0.275206
6	1	-0.751191	-0.366971	-0.262215
7	8	-1.519938	-1.143642	0.168234
8	8	-2.780718	-0.512709	0.047143
9	1	-2.928717	-0.175078	0.942039
10	1	2.947532	-1.407374	-0.366877
11	1	1.984200	-1.100561	-1.817390
12	1	1.270091	-1.962501	-0.449349
13	1	2.191638	0.962986	-0.434578
14	1	2.476724	-0.163821	1.776469
15	1	0.761497	-0.601816	1.777394
16	1	1.249128	1.097165	1.859711
17	1	0.051563	0.407735	-1.772975
18	1	0.059913	2.745165	-0.667770
19	1	-0.549364	1.999269	0.811329
20	1	-1.526712	1.969871	-0.663332

4 6

4 15

1 2 3 5 10 11 12 13 14 15 16 17 18 19 20

6 3

7 8 9

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad b3lyp/6-31g^*$$

0 0 1

1

100

3

0.5

0. 0.

0. 0.

0.5 0.

8

298.15 300. 400. 500. 600. 800. 1000. 1500.

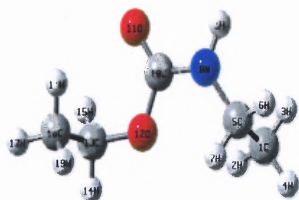
SECTION II

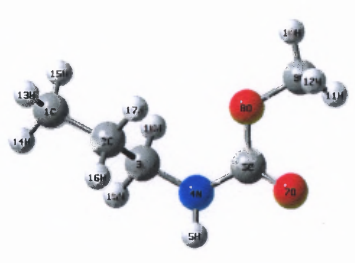
APPENDIX B

Appendix B has two parts. Illustrations of the optimized structures of the molecules and radicals optimized at the B3LYP/6-31G(d,p) density functional calculation level along with the geometry parameters are presented in Section B.1 of Appendix B. Bond length or the distance between two atoms is in Angstroms and the bond angle and the dihedral angle are in degrees. Section B.2 contains the SMCPS files used in the calculation of entropies (S_{298}^0) and heat capacities ($C_p(T)$) at the B3LYP/6-31G(d,p) level.

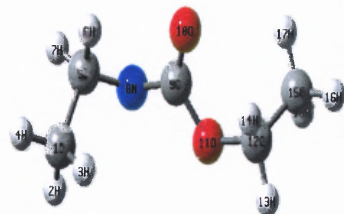
B.1 Geometry Parameters^a Calculated at the B3LYP/6-31G(d,p) Level

B.1.1 CCNCO ₂ CC			
			R1 R(1,2) 1.0935
			R2 R(1,3) 1.095
			R3 R(1,4) 1.0953
			R4 R(1,5) 1.5315
			R5 R(5,6) 1.0953
			R6 R(5,7) 1.0921
			R7 R(5,8) 1.4593
			R8 R(8,9) 1.0091
			R9 R(8,10) 1.3655
			R10 R(10,11) 1.2195
			R11 R(10,12) 1.362
			R12 R(12,13) 1.4445
			R13 R(13,14) 1.093
			R14 R(13,15) 1.0924
			R15 R(13,16) 1.5207
			R16 R(16,17) 1.0953
			R17 R(16,18) 1.0925
			R18 R(16,19) 1.0941
			A1 A(2,1,3) 108.299
			A2 A(2,1,4) 108.2728
			A3 A(2,1,5) 110.3773
			A4 A(3,1,4) 108.0536
			A5 A(3,1,5) 111.2095
			A6 A(4,1,5) 110.5313
			A7 A(1,5,6) 110.3486
			A8 A(1,5,7) 110.174
			A9 A(1,5,8) 113.9487
			A10 A(6,5,7) 107.0958
			A11 A(6,5,8) 107.2037
			A12 A(7,5,8) 107.7908
			A13 A(5,8,9) 118.8948
			A14 A(5,8,10) 126.0361
			A15 A(9,8,10) 112.9082
			A16 A(8,10,11) 124.2338
			A17 A(8,10,12) 111.2172
			A18 A(11,10,12) 124.5434
			A19 A(10,12,13) 115.4784
			A20 A(12,13,14) 104.3256
			A21 A(12,13,15) 108.8252
			A22 A(12,13,16) 111.5604
			A23 A(14,13,15) 109.4017
			A24 A(14,13,16) 111.4854
			A25 A(15,13,16) 111.0052
			A26 A(13,16,17) 109.9256
			A27 A(13,16,18) 110.2759
			A28 A(13,16,19) 110.9384
			A29 A(17,16,18) 108.3185
			A30 A(17,16,19) 108.2954
			A31 A(18,16,19) 109.0213
D1	D(2,1,5,6)	178.3167	
D2	D(2,1,5,7)	60.2633	
D3	D(2,1,5,8)	-61.0263	
D4	D(3,1,5,6)	-61.457	
D5	D(3,1,5,7)	-179.5103	
D6	D(3,1,5,8)	59.2001	
D7	D(4,1,5,6)	58.5633	
D8	D(4,1,5,7)	-59.4901	
D9	D(4,1,5,8)	179.2203	
D10	D(1,5,8,9)	-81.9205	
D11	D(1,5,8,10)	80.1311	
D12	D(6,5,8,9)	40.4796	
D13	D(6,5,8,10)	-157.4688	
D14	D(7,5,8,9)	155.4752	
D15	D(7,5,8,10)	-42.4733	
D16	D(5,8,10,11)	-171.0191	
D17	D(5,8,10,12)	9.8128	
D18	D(9,8,10,11)	-8.0506	
D19	D(9,8,10,12)	172.7812	
D20	D(8,10,12,13)	176.7919	
D21	D(11,10,12,13)	-2.3731	
D22	D(10,12,13,14)	155.7142	
D23	D(10,12,13,15)	39.0163	
D24	D(10,12,13,16)	-83.7974	
D25	D(12,13,16,17)	-176.0251	
D26	D(12,13,16,18)	64.6135	
D27	D(12,13,16,19)	-56.2751	
D28	D(14,13,16,17)	-59.8291	
D29	D(14,13,16,18)	-179.1904	
D30	D(14,13,16,19)	59.9209	
D31	D(15,13,16,17)	62.4161	
D32	D(15,13,16,18)	-56.9452	
D33	D(15,13,16,19)	-177.8338	

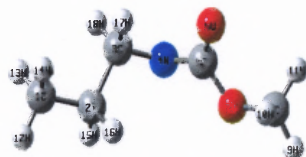


B.1.2 CCCNCO ₂ C					
			R1	R(1,2)	1.5311
			R2	R(1,13)	1.0941
			R3	R(1,14)	1.0961
			R4	R(1,15)	1.0958
			R5	R(2,3)	1.535
			R6	R(2,16)	1.0978
			R7	R(2,17)	1.096
			R8	R(3,4)	1.458
			R9	R(3,18)	1.0931
			R10	R(3,19)	1.0964
			R11	R(4,5)	1.0089
			R12	R(4,6)	1.3653
			R13	R(6,7)	1.2183
			R14	R(6,8)	1.3624
			R15	R(8,9)	1.4332
			R16	R(9,10)	1.0904
			R17	R(9,11)	1.0929
			R18	R(9,12)	1.0927
D1	D(13,1,2,3)	-179.8996	A1	A(2,1,13)	111.2056
D2	D(13,1,2,16)	58.3349	A2	A(2,1,14)	111.4212
D3	D(13,1,2,17)	-58.9288	A3	A(2,1,15)	111.2644
D4	D(14,1,2,3)	60.0865	A4	A(13,1,14)	107.579
D5	D(14,1,2,16)	-61.6791	A5	A(13,1,15)	107.6135
D6	D(14,1,2,17)	-178.9428	A6	A(14,1,15)	107.5634
D7	D(15,1,2,3)	-59.9475	A7	A(1,2,3)	112.3637
D8	D(15,1,2,16)	178.287	A8	A(1,2,16)	109.961
D9	D(15,1,2,17)	61.0233	A9	A(1,2,17)	110.1336
D10	D(1,2,3,4)	-179.3607	A10	A(3,2,16)	109.1299
D11	D(1,2,3,18)	59.0792	A11	A(3,2,17)	108.4121
D12	D(1,2,3,19)	-58.488	A12	A(16,2,17)	106.6635
D13	D(16,2,3,4)	-57.1231	A13	A(2,3,4)	114.2047
D14	D(16,2,3,18)	-178.6831	A14	A(2,3,18)	109.9604
D15	D(16,2,3,19)	63.7497	A15	A(2,3,19)	110.0153
D16	D(17,2,3,4)	58.6847	A16	A(4,3,18)	107.9834
D17	D(17,2,3,18)	-62.8753	A17	A(4,3,19)	107.423
D18	D(17,2,3,19)	179.5575	A18	A(18,3,19)	106.9702
D19	D(2,3,4,5)	81.7839	A19	A(3,4,5)	118.9754
D20	D(2,3,4,6)	-81.1716	A20	A(3,4,6)	126.1238
D21	D(18,3,4,5)	-155.5725	A21	A(5,4,6)	112.9552
D22	D(18,3,4,6)	41.4719	A22	A(4,6,7)	124.6373
D23	D(19,3,4,5)	-40.5176	A23	A(4,6,8)	111.3328
D24	D(19,3,4,6)	156.5269	A24	A(7,6,8)	124.0214
D25	D(3,4,6,7)	171.7322	A25	A(6,8,9)	114.3447
D26	D(3,4,6,8)	-9.2927	A26	A(8,9,10)	105.5554
D27	D(5,4,6,7)	7.9015	A27	A(8,9,11)	110.8598
D28	D(5,4,6,8)	-173.1234	A28	A(8,9,12)	110.8732
D29	D(4,6,8,9)	-177.5995	A29	A(10,9,11)	110.38
D30	D(7,6,8,9)	1.3831	A30	A(10,9,12)	110.4775
D31	D(6,8,9,10)	-179.0865	A31	A(11,9,12)	108.6844
D32	D(6,8,9,11)	61.3812			
D33	D(6,8,9,12)	-59.43028			

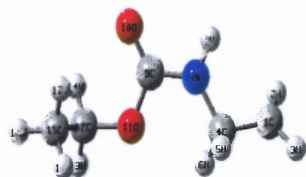
B.1.3 <chem>CCN;CO2CC</chem>					
			R1	R(1,2)	1.0929
			R2	R(1,3)	1.0938
			R3	R(1,4)	1.0938
			R4	R(1,5)	1.5436
			R5	R(5,6)	1.0978
			R6	R(5,7)	1.0945
			R7	R(5,8)	1.4465
			R8	R(8,9)	1.3907
			R9	R(9,10)	1.2221
			R10	R(9,11)	1.3443
			R11	R(11,12)	1.4497
			R12	R(12,13)	1.0923
			R13	R(12,14)	1.0929
			R14	R(12,15)	1.5203
			R15	R(15,16)	1.0951
			R16	R(15,17)	1.0925
			R17	R(15,18)	1.0936
			A1	A(2,1,3)	108.4965
			A2	A(2,1,4)	108.6499
			A3	A(2,1,5)	110.827
			A4	A(3,1,4)	108.3918
			A5	A(3,1,5)	111.0583
			A6	A(4,1,5)	109.35
			A7	A(1,5,6)	109.6112
			A8	A(1,5,7)	109.2728
			A9	A(1,5,8)	110.3656
			A10	A(6,5,7)	109.1735
			A11	A(6,5,8)	110.2768
			A12	A(7,5,8)	108.1088
			A13	A(5,8,9)	115.3603
			A14	A(8,9,10)	123.7824
			A15	A(8,9,11)	110.8035
			A16	A(10,9,11)	125.2464
			A17	A(9,11,12)	116.1182
			A18	A(11,12,13)	104.1114
			A19	A(11,12,14)	109.0037
			A20	A(11,12,15)	111.2462
			A21	A(13,12,14)	109.3959
			A22	A(13,12,15)	111.6355
			A23	A(14,12,15)	111.1909
			A24	A(12,15,16)	109.7437
			A25	A(12,15,17)	110.5238
			A26	A(12,15,18)	110.8163
			A27	A(16,15,17)	108.3131
			A28	A(16,15,18)	108.3761
			A29	A(17,15,18)	109.0024
D1	D(2,1,5,6)	-177.8556			
D2	D(2,1,5,7)	62.5444			
D3	D(2,1,5,8)	-56.2082			
D4	D(3,1,5,6)	-57.1796			
D5	D(3,1,5,7)	-176.7795			
D6	D(3,1,5,8)	64.4678			
D7	D(4,1,5,6)	62.3945			
D8	D(4,1,5,7)	-57.2054			
D9	D(4,1,5,8)	-175.9581			
D10	D(1,5,8,9)	-90.1472			
D11	D(6,5,8,9)	31.1054			
D12	D(7,5,8,9)	150.3929			
D13	D(5,8,9,10)	-47.7658			
D14	D(5,8,9,11)	136.7279			
D15	D(8,9,11,12)	176.1123			
D16	D(10,9,11,12)	0.6858			
D17	D(9,11,12,13)	155.06			
D18	D(9,11,12,14)	38.3968			
D19	D(9,11,12,15)	-84.5661			
D20	D(11,12,15,16)	-175.7286			
D21	D(11,12,15,17)	64.8767			
D22	D(11,12,15,18)	-56.0728			
D23	D(13,12,15,16)	-59.9032			
D24	D(13,12,15,17)	-179.2978			
D25	D(13,12,15,18)	59.7526			
D26	D(14,12,15,16)	62.573			
D27	D(14,12,15,17)	-56.8217			
D28	D(14,12,15,18)	-177.7712			

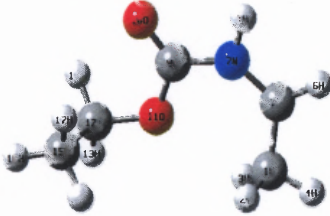


B.1.4 CCCN ₃ CO ₂ C					
			R1	R(1,2)	1.5308
			R2	R(1,12)	1.0942
			R3	R(1,13)	1.0952
			R4	R(1,14)	1.0951
			R5	R(2,3)	1.55
			R6	R(2,15)	1.0952
			R7	R(2,16)	1.0964
			R8	R(3,4)	1.4432
			R9	R(3,17)	1.0982
			R10	R(3,18)	1.0957
			R11	R(4,5)	1.3902
			R12	R(5,6)	1.2213
			R13	R(5,7)	1.3455
			R14	R(7,8)	1.4372
			R15	R(8,9)	1.0896
			R16	R(8,10)	1.0929
			R17	R(8,11)	1.0928
			A1	A(2,1,12)	110.6808
			A2	A(2,1,13)	111.2856
			A3	A(2,1,14)	111.4162
			A4	A(12,1,13)	107.7168
			A5	A(12,1,14)	107.7841
			A6	A(13,1,14)	107.7936
			A7	A(1,2,3)	111.629
			A8	A(1,2,15)	110.4023
			A9	A(1,2,16)	110.1568
			A10	A(3,2,15)	108.7732
			A11	A(3,2,16)	108.9029
			A12	A(15,2,16)	106.8405
			A13	A(2,3,4)	110.3984
			A14	A(2,3,17)	109.375
			A15	A(2,3,18)	108.7145
			A16	A(4,3,17)	110.8796
			A17	A(4,3,18)	108.2287
			A18	A(17,3,18)	109.2001
			A19	A(3,4,5)	115.4055
			A20	A(4,5,6)	124.3806
			A21	A(4,5,7)	110.8433
			A22	A(6,5,7)	124.592
			A23	A(5,7,8)	114.9487
			A24	A(7,8,9)	105.4925
			A25	A(7,8,10)	110.8804
			A26	A(7,8,11)	110.5042
			A27	A(9,8,10)	110.5832
			A28	A(9,8,11)	110.5141
			A29	A(10,8,11)	108.8483
D1	D(12,1,2,3)	179.9596			
D2	D(12,1,2,15)	58.8384			
D3	D(12,1,2,16)	-58.9233			
D4	D(13,1,2,3)	60.2138			
D5	D(13,1,2,15)	-60.9074			
D6	D(13,1,2,16)	-178.6691			
D7	D(14,1,2,3)	-60.1238			
D8	D(14,1,2,15)	178.7551			
D9	D(14,1,2,16)	60.9933			
D10	D(1,2,3,4)	-175.6568			
D11	D(1,2,3,17)	62.0773			
D12	D(1,2,3,18)	-57.0795			
D13	D(15,2,3,4)	-53.593			
D14	D(15,2,3,17)	-175.8589			
D15	D(15,2,3,18)	64.9842			
D16	D(16,2,3,4)	62.4997			
D17	D(16,2,3,17)	-59.7662			
D18	D(16,2,3,18)	-178.923			
D19	D(2,3,4,5)	-93.5349			
D20	D(17,3,4,5)	27.8423			
D21	D(18,3,4,5)	147.5918			
D22	D(3,4,5,6)	-45.8809			
D23	D(3,4,5,7)	138.8627			
D24	D(4,5,7,8)	176.6178			
D25	D(6,5,7,8)	1.3734			
D26	D(5,7,8,9)	176.6204			
D27	D(5,7,8,10)	56.8713			
D28	D(5,7,8,11)	-63.9136			

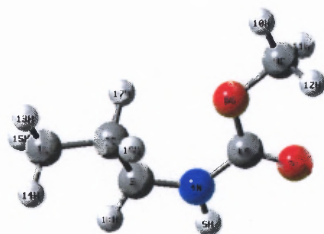


B.1.5 C ₇ CNCO ₂ CC					
			R1	R(1,2)	1.0848
			R2	R(1,3)	1.0838
			R3	R(1,4)	1.4887
			R4	R(4,5)	1.1016
			R5	R(4,6)	1.0992
			R6	R(4,7)	1.4591
			R7	R(7,8)	1.0092
			R8	R(7,9)	1.3652
			R9	R(9,10)	1.2195
			R10	R(9,11)	1.3609
			R11	R(11,12)	1.4453
			R12	R(12,13)	1.0929
			R13	R(12,14)	1.0923
			R14	R(12,15)	1.5205
			R15	R(15,16)	1.0952
			R16	R(15,17)	1.0923
			R17	R(15,18)	1.0942
			A1	A(2,1,3)	118.79
			A2	A(2,1,4)	119.9614
			A3	A(3,1,4)	120.3387
			A4	A(1,4,5)	110.1288
			A5	A(1,4,6)	111.1821
			A6	A(1,4,7)	111.4249
			A7	A(5,4,6)	105.8012
			A8	A(5,4,7)	111.2736
			A9	A(6,4,7)	106.8496
			A10	A(4,7,8)	118.2023
			A11	A(4,7,9)	126.9809
			A12	A(8,7,9)	113.5607
			A13	A(7,9,10)	123.9628
			A14	A(7,9,11)	111.4597
			A15	A(10,9,11)	124.57
			A16	A(9,11,12)	115.4954
			A17	A(11,12,13)	104.3195
			A18	A(11,12,14)	108.8337
			A19	A(11,12,15)	111.5078
			A20	A(13,12,14)	109.4102
			A21	A(13,12,15)	111.5133
			A22	A(14,12,15)	111.0182
			A23	A(12,15,16)	109.9152
			A24	A(12,15,17)	110.2198
			A25	A(12,15,18)	110.928
			A26	A(16,15,17)	108.3619
			A27	A(16,15,18)	108.2864
			A28	A(17,15,18)	109.0662
D1	D(2,1,4,5)	-162.023			
D2	D(2,1,4,6)	81.0368			
D3	D(2,1,4,7)	-38.0411			
D4	D(3,1,4,5)	29.0246			
D5	D(3,1,4,6)	-87.9156			
D6	D(3,1,4,7)	153.0064			
D7	D(1,4,7,8)	-44.4657			
D8	D(1,4,7,9)	149.2233			
D9	D(5,4,7,8)	78.8664			
D10	D(5,4,7,9)	-87.4446			
D11	D(6,4,7,8)	-166.0942			
D12	D(6,4,7,9)	27.5947			
D13	D(4,7,9,10)	173.8618			
D14	D(4,7,9,11)	-7.0982			
D15	D(8,7,9,10)	7.0131			
D16	D(8,7,9,11)	-173.9469			
D17	D(7,9,11,12)	-178.9068			
D18	D(10,9,11,12)	0.1263			
D19	D(9,11,12,13)	155.3028			
D20	D(9,11,12,14)	38.5943			
D21	D(9,11,12,15)	-84.207			
D22	D(11,12,15,16)	-175.9527			
D23	D(11,12,15,17)	64.6738			
D24	D(11,12,15,18)	-56.2271			
D25	D(13,12,15,16)	-59.7799			
D26	D(13,12,15,17)	-179.1534			
D27	D(13,12,15,18)	59.9457			
D28	D(14,12,15,16)	62.5051			
D29	D(14,12,15,17)	-56.8684			
D30	D(14,12,15,18)	-177.7693			

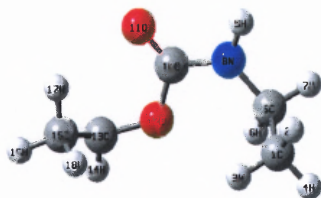


B.1.6 CC _j NCO ₂ CC					
			R1	R(1,2)	1.1014
			R2	R(1,3)	1.0946
			R3	R(1,4)	1.0934
			R4	R(1,5)	1.4898
			R5	R(5,6)	1.0829
			R6	R(5,7)	1.3969
			R7	R(7,8)	1.0104
			R8	R(7,9)	1.3762
			R9	R(9,10)	1.2215
			R10	R(9,11)	1.354
			R11	R(11,12)	1.4467
			R12	R(12,13)	1.0927
			R13	R(12,14)	1.0921
			R14	R(12,15)	1.5204
			R15	R(15,16)	1.0952
			R16	R(15,17)	1.0925
			R17	R(15,18)	1.094
D1	D(2,1,5,6)	102.206	A1	A(2,1,3)	106.3815
D2	D(2,1,5,7)	-56.1751	A2	A(2,1,4)	107.742
D3	D(3,1,5,6)	-137.3936	A3	A(2,1,5)	112.5709
D4	D(3,1,5,7)	64.2252	A4	A(3,1,4)	108.2761
D5	D(4,1,5,6)	-17.1862	A5	A(3,1,5)	112.7998
D6	D(4,1,5,7)	-175.5673	A6	A(4,1,5)	108.8663
D7	D(1,5,7,8)	164.8558	A7	A(1,5,6)	120.1345
D8	D(1,5,7,9)	-21.8303	A8	A(1,5,7)	124.2463
D9	D(6,5,7,8)	5.0254	A9	A(6,5,7)	112.4638
D10	D(6,5,7,9)	178.3393	A10	A(5,7,8)	116.7912
D11	D(5,7,9,10)	-177.8	A11	A(5,7,9)	132.5961
D12	D(5,7,9,11)	2.1584	A12	A(8,7,9)	110.3394
D13	D(8,7,9,10)	-4.1639	A13	A(7,9,10)	122.3978
D14	D(8,7,9,11)	175.7945	A14	A(7,9,11)	112.5593
D15	D(7,9,11,12)	178.325	A15	A(10,9,11)	125.0428
D16	D(10,9,11,12)	-1.7179	A16	A(9,11,12)	115.4625
D17	D(9,11,12,13)	155.6778	A17	A(11,12,13)	104.1647
D18	D(9,11,12,14)	39.0505	A18	A(11,12,14)	108.801
D19	D(9,11,12,15)	-83.8838	A19	A(11,12,15)	111.539
D20	D(11,12,15,16)	-175.87	A20	A(13,12,14)	109.4211
D21	D(11,12,15,17)	64.7915	A21	A(13,12,15)	111.5347
D22	D(11,12,15,18)	-56.1852	A22	A(14,12,15)	111.1252
D23	D(13,12,15,16)	-59.857	A23	A(12,15,16)	109.8436
D24	D(13,12,15,17)	-179.1954	A24	A(12,15,17)	110.3642
D25	D(13,12,15,18)	59.8278	A25	A(12,15,18)	110.9273
D26	D(14,12,15,16)	62.5331	A26	A(16,15,17)	108.2971
D27	D(14,12,15,17)	-56.8054	A27	A(16,15,18)	108.2913
D28	D(14,12,15,18)	-177.7821	A28	A(17,15,18)	109.0503

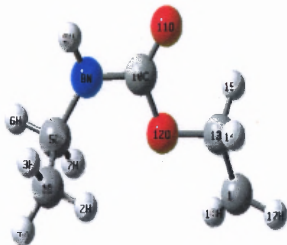
B.1.7 CCC _j NCO ₂ C					
			R1	R(1,2)	1.5334
			R2	R(1,13)	1.0938
			R3	R(1,14)	1.0956
			R4	R(1,15)	1.095
			R5	R(2,3)	1.4947
			R6	R(2,16)	1.1032
			R7	R(2,17)	1.0964
			R8	R(3,4)	1.397
			R9	R(3,18)	1.0843
			R10	R(4,5)	1.0103
			R11	R(4,6)	1.3757
			R12	R(6,7)	1.2203
			R13	R(6,8)	1.3547
			R14	R(8,9)	1.435
			R15	R(9,10)	1.0901
			R16	R(9,11)	1.0925
			R17	R(9,12)	1.0927
			A1	A(2,1,13)	110.8932
			A2	A(2,1,14)	111.3315
			A3	A(2,1,15)	111.0796
			A4	A(13,1,14)	107.7402
			A5	A(13,1,15)	107.903
			A6	A(14,1,15)	107.7358
			A7	A(1,2,3)	111.2247
			A8	A(1,2,16)	109.5259
			A9	A(1,2,17)	109.7856
			A10	A(3,2,16)	110.5203
			A11	A(3,2,17)	110.6813
			A12	A(16,2,17)	104.915
			A13	A(2,3,4)	124.6479
			A14	A(2,3,18)	119.5131
			A15	A(4,3,18)	112.486
			A16	A(3,4,5)	116.7762
			A17	A(3,4,6)	132.6274
			A18	A(5,4,6)	110.3293
			A19	A(4,6,7)	122.8292
			A20	A(4,6,8)	112.6813
			A21	A(7,6,8)	124.4891
			A22	A(6,8,9)	114.2824
			A23	A(8,9,10)	105.4581
			A24	A(8,9,11)	110.7556
			A25	A(8,9,12)	110.7844
			A26	A(10,9,11)	110.52
			A27	A(10,9,12)	110.5016
			A28	A(11,9,12)	108.8047
D1	D(13,1,2,3)	-179.5504			
D2	D(13,1,2,16)	57.989			
D3	D(13,1,2,17)	-56.7067			
D4	D(14,1,2,3)	60.5022			
D5	D(14,1,2,16)	-61.9584			
D6	D(14,1,2,17)	-176.654			
D7	D(15,1,2,3)	-59.565			
D8	D(15,1,2,16)	177.9744			
D9	D(15,1,2,17)	63.2788			
D10	D(1,2,3,4)	-175.4025			
D11	D(1,2,3,18)	-17.6692			
D12	D(16,2,3,4)	-53.5179			
D13	D(16,2,3,18)	104.2153			
D14	D(17,2,3,4)	62.2703			
D15	D(17,2,3,18)	-139.9965			
D16	D(2,3,4,5)	164.8492			
D17	D(2,3,4,6)	-21.762			
D18	D(18,3,4,5)	5.7581			
D19	D(18,3,4,6)	179.147			
D20	D(3,4,6,7)	-177.7423			
D21	D(3,4,6,8)	2.4767			
D22	D(5,4,6,7)	-4.0354			
D23	D(5,4,6,8)	176.1837			
D24	D(4,6,8,9)	179.2212			
D25	D(7,6,8,9)	-0.5555			
D26	D(6,8,9,10)	179.8714			
D27	D(6,8,9,11)	60.2851			
D28	D(6,8,9,12)	-60.5489			



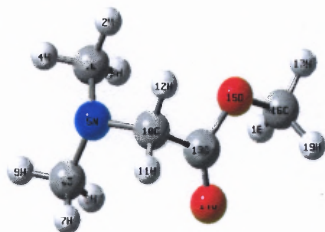
B.1.8 CCNCO ₂ C ₃ C					
			R1	R(1,2)	1.0949
			R2	R(1,3)	1.0936
			R3	R(1,4)	1.0952
			R4	R(1,5)	1.5313
			R5	R(5,6)	1.0919
			R6	R(5,7)	1.0952
			R7	R(5,8)	1.4597
			R8	R(8,9)	1.0089
			R9	R(8,10)	1.364
			R10	R(10,11)	1.2152
			R11	R(10,12)	1.3748
			R12	R(12,13)	1.3884
			R13	R(13,14)	1.085
			R14	R(13,15)	1.4884
			R15	R(15,16)	1.0938
			R16	R(15,17)	1.0923
			R17	R(15,18)	1.1033
D1	D(2,1,5,6)	179.4861	A1	A(2,1,3)	108.2778
D2	D(2,1,5,7)	61.4441	A2	A(2,1,4)	108.0937
D3	D(2,1,5,8)	-58.9609	A3	A(2,1,5)	111.1897
D4	D(3,1,5,6)	-60.2661	A4	A(3,1,4)	108.2412
D5	D(3,1,5,7)	-178.3081	A5	A(3,1,5)	110.4691
D6	D(3,1,5,8)	61.287	A6	A(4,1,5)	110.4712
D7	D(4,1,5,6)	59.4684	A7	A(1,5,6)	110.275
D8	D(4,1,5,7)	-58.5736	A8	A(1,5,7)	110.3114
D9	D(4,1,5,8)	-178.9785	A9	A(1,5,8)	113.8448
D10	D(1,5,8,9)	84.4219	A10	A(6,5,7)	107.0546
D11	D(1,5,8,10)	-81.6006	A11	A(6,5,8)	107.9918
D12	D(6,5,8,9)	-152.7662	A12	A(7,5,8)	107.0855
D13	D(6,5,8,10)	41.2113	A13	A(5,8,9)	119.0176
D14	D(7,5,8,9)	-37.7789	A14	A(5,8,10)	126.812
D15	D(7,5,8,10)	156.1986	A15	A(9,8,10)	112.875
D16	D(5,8,10,11)	173.0877	A16	A(8,10,11)	124.6432
D17	D(5,8,10,12)	-8.3193	A17	A(8,10,12)	110.2124
D18	D(9,8,10,11)	6.3406	A18	A(11,10,12)	125.1281
D19	D(9,8,10,12)	-175.0664	A19	A(10,12,13)	120.1124
D20	D(8,10,12,13)	178.1018	A20	A(12,13,14)	109.3218
D21	D(11,10,12,13)	-3.3135	A21	A(12,13,15)	121.0203
D22	D(10,12,13,14)	158.967	A22	A(14,13,15)	121.3889
D23	D(10,12,13,15)	-52.2861	A23	A(13,15,16)	109.2084
D24	D(12,13,15,16)	-176.1856	A24	A(13,15,17)	111.5679
D25	D(12,13,15,17)	62.959	A25	A(13,15,18)	111.7112
D26	D(12,13,15,18)	-57.3282	A26	A(16,15,17)	109.2363
D27	D(14,13,15,16)	-31.1826	A27	A(16,15,18)	107.5611
D28	D(14,13,15,17)	-152.038	A28	A(17,15,18)	107.4435
D29	D(14,13,15,18)	87.6748			

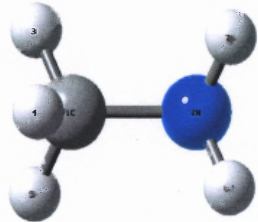


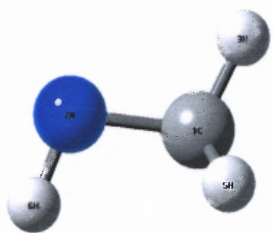
B.1.9 CCNCO ₂ CC _j					
			R1	R(1,2)	1.0934
			R2	R(1,3)	1.095
			R3	R(1,4)	1.0953
			R4	R(1,5)	1.5313
			R5	R(5,6)	1.0952
			R6	R(5,7)	1.0922
			R7	R(5,8)	1.4596
			R8	R(8,9)	1.009
			R9	R(8,10)	1.3654
			R10	R(10,11)	1.2189
			R11	R(10,12)	1.3621
			R12	R(12,13)	1.4433
			R13	R(13,14)	1.0977
			R14	R(13,15)	1.1016
			R15	R(13,16)	1.4801
			R16	R(16,17)	1.0834
			R17	R(16,18)	1.0837
			A1	A(2,1,3)	108.3602
			A2	A(2,1,4)	108.2581
			A3	A(2,1,5)	110.341
			A4	A(3,1,4)	108.0689
			A5	A(3,1,5)	111.2164
			A6	A(4,1,5)	110.5011
			A7	A(1,5,6)	110.3757
			A8	A(1,5,7)	110.1493
			A9	A(1,5,8)	113.9774
			A10	A(6,5,7)	107.0475
			A11	A(6,5,8)	107.1282
			A12	A(7,5,8)	107.8786
			A13	A(5,8,9)	118.9186
			A14	A(5,8,10)	125.99
			A15	A(9,8,10)	112.9304
			A16	A(8,10,11)	124.5219
			A17	A(8,10,12)	111.2613
			A18	A(11,10,12)	124.2095
			A19	A(10,12,13)	114.8269
			A20	A(12,13,14)	109.4594
			A21	A(12,13,15)	108.2725
			A22	A(12,13,16)	108.4283
			A23	A(14,13,15)	105.974
			A24	A(14,13,16)	111.9102
			A25	A(15,13,16)	112.7008
			A26	A(13,16,17)	119.8418
			A27	A(13,16,18)	120.1252
			A28	A(17,16,18)	119.0748
D1	D(2,1,5,6)	178.3151			
D2	D(2,1,5,7)	60.3198			
D3	D(2,1,5,8)	-61.0857			
D4	D(3,1,5,6)	-61.4012			
D5	D(3,1,5,7)	-179.3966			
D6	D(3,1,5,8)	59.1979			
D7	D(4,1,5,6)	58.6226			
D8	D(4,1,5,7)	-59.3727			
D9	D(4,1,5,8)	179.2218			
D10	D(1,5,8,9)	-82.922			
D11	D(1,5,8,10)	79.1334			
D12	D(6,5,8,9)	39.4767			
D13	D(6,5,8,10)	-158.4679			
D14	D(7,5,8,9)	154.4217			
D15	D(7,5,8,10)	-43.523			
D16	D(5,8,10,11)	-171.2181			
D17	D(5,8,10,12)	9.7307			
D18	D(9,8,10,11)	-8.245			
D19	D(9,8,10,12)	172.7039			
D20	D(8,10,12,13)	178.2255			
D21	D(11,10,12,13)	-0.8292			
D22	D(10,12,13,14)	68.2037			
D23	D(10,12,13,15)	-46.8859			
D24	D(10,12,13,16)	-169.4606			
D25	D(12,13,16,17)	-158.2808			
D26	D(12,13,16,18)	33.0209			
D27	D(14,13,16,17)	-37.4503			
D28	D(14,13,16,18)	153.8513			
D29	D(15,13,16,17)	81.8763			
D30	D(15,13,16,18)	-86.8221			

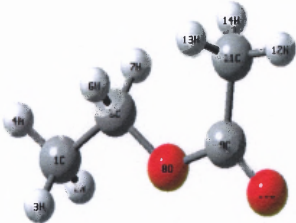


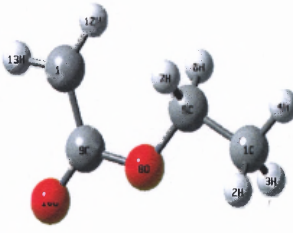
B.1.10 C ₂ NCCO ₂ C					
			R1	R(1,2)	1.0943
			R2	R(1,3)	1.105
			R3	R(1,4)	1.0949
			R4	R(1,5)	1.4574
			R5	R(5,6)	1.4593
			R6	R(5,10)	1.4605
			R7	R(6,7)	1.0941
			R8	R(6,8)	1.1025
			R9	R(6,9)	1.0951
			R10	R(10,11)	1.0944
			R11	R(10,12)	1.0939
			R12	R(10,13)	1.5308
			R13	R(13,14)	1.2135
			R14	R(13,15)	1.3541
			R15	R(15,16)	1.4385
			R16	R(16,17)	1.0897
			R17	R(16,18)	1.0926
			R18	R(16,19)	1.0927
			A1	A(2,1,3)	107.828
			A2	A(2,1,4)	108.1679
			A3	A(2,1,5)	109.7088
			A4	A(3,1,4)	107.7157
			A5	A(3,1,5)	114.2394
			A6	A(4,1,5)	109.0045
			A7	A(1,5,6)	112.5919
			A8	A(1,5,10)	113.8144
			A9	A(6,5,10)	114.0547
			A10	A(5,6,7)	109.5519
			A11	A(5,6,8)	114.0357
			A12	A(5,6,9)	108.8112
			A13	A(7,6,8)	107.728
			A14	A(7,6,9)	108.2195
			A15	A(8,6,9)	108.3418
			A16	A(5,10,11)	108.4946
			A17	A(5,10,12)	108.8004
			A18	A(5,10,13)	113.9526
			A19	A(11,10,12)	109.0103
			A20	A(11,10,13)	107.1335
			A21	A(12,10,13)	109.3461
			A22	A(10,13,14)	124.906
			A23	A(10,13,15)	111.6523
			A24	A(14,13,15)	123.3427
			A25	A(13,15,16)	115.2471
			A26	A(15,16,17)	105.7545
			A27	A(15,16,18)	110.5861
			A28	A(15,16,19)	110.5527
			A29	A(17,16,18)	110.6471
			A30	A(17,16,19)	110.5828
			A31	A(18,16,19)	108.7092
D1	D(2,1,5,6)	176.7381			
D2	D(2,1,5,10)	-51.486			
D3	D(3,1,5,6)	-62.0675			
D4	D(3,1,5,10)	69.7084			
D5	D(4,1,5,6)	58.4648			
D6	D(4,1,5,10)	-169.7593			
D7	D(1,5,6,7)	-176.4328			
D8	D(1,5,6,8)	62.7574			
D9	D(1,5,6,9)	-58.3019			
D10	D(10,5,6,7)	51.911			
D11	D(10,5,6,8)	-68.8989			
D12	D(10,5,6,9)	170.0419			
D13	D(1,5,10,11)	174.6565			
D14	D(1,5,10,12)	56.1858			
D15	D(1,5,10,13)	-66.1009			
D16	D(6,5,10,11)	-54.2826			
D17	D(6,5,10,12)	-172.7532			
D18	D(6,5,10,13)	64.9601			
D19	D(5,10,13,14)	-78.3025			
D20	D(5,10,13,15)	98.1716			
D21	D(11,10,13,14)	41.7093			
D22	D(11,10,13,15)	-141.8167			
D23	D(12,10,13,14)	159.7112			
D24	D(12,10,13,15)	-23.8148			
D25	D(10,13,15,16)	-176.6462			
D26	D(14,13,15,16)	-0.1075			
D27	D(13,15,16,17)	179.6364			
D28	D(13,15,16,18)	59.813			
D29	D(13,15,16,19)	-60.6354			

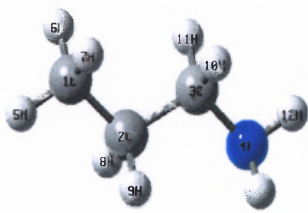


B.1.11 CH ₃ NH ₂			
	R1	R(1,2)	1.4641
	R2	R(1,3)	1.0949
	R3	R(1,4)	1.1036
	R4	R(1,5)	1.0949
	R5	R(2,6)	1.0172
	R6	R(2,7)	1.0172
	A1	A(2,1,3)	109.2495
	A2	A(2,1,4)	115.8558
	A3	A(2,1,5)	109.2461
	A4	A(3,1,4)	107.5521
	A5	A(3,1,5)	107.0295
	A6	A(4,1,5)	107.5512
	A7	A(1,2,6)	109.7501
	A8	A(1,2,7)	109.7467
	A9	A(6,2,7)	105.8453
	D1	D(3,1,2,6)	179.5719
D2	D(3,1,2,7)	63.6518	
D3	D(4,1,2,6)	57.9576	
D4	D(4,1,2,7)	-57.9625	
D5	D(5,1,2,6)	-63.6529	
D6	D(5,1,2,7)	-179.5729	

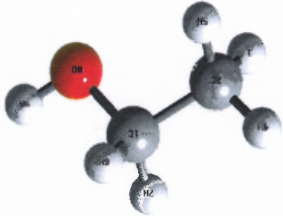
B.1.12 CH ₃ N ₂ H			
	R1	R(1,2)	1.4439
	R2	R(1,3)	1.0939
	R3	R(1,4)	1.1035
	R4	R(1,5)	1.1035
	R5	R(2,6)	1.0313
	A1	A(2,1,3)	110.5642
	A2	A(2,1,4)	111.8021
	A3	A(2,1,5)	111.7606
	A4	A(3,1,4)	108.3966
	A5	A(3,1,5)	108.3805
	A6	A(4,1,5)	105.736
	A7	A(1,2,6)	105.944
	D1	D(3,1,2,6)	179.8797
	D2	D(4,1,2,6)	59.0086
	D3	D(5,1,2,6)	-59.2977
	D6	D(5,1,2,7)	-179.5729

B.1.13 CCOC(O)C			
	R1	R(1,2)	1.0931
	R2	R(1,3)	1.0931
	R3	R(1,4)	1.0944
	R4	R(1,5)	1.5182
	R5	R(5,6)	1.097
	R6	R(5,7)	1.097
	R7	R(5,8)	1.4379
	R8	R(8,9)	1.3619
	R9	R(9,10)	1.2068
	R10	R(9,11)	1.5166
	R11	R(11,12)	1.0889
	R12	R(11,13)	1.0946
	R13	R(11,14)	1.0946
	D1	D(2,1,5,6)	179.866
	D2	D(2,1,5,7)	60.1394
	D3	D(2,1,5,8)	-59.9931
	D4	D(3,1,5,6)	-60.1236
	D5	D(3,1,5,7)	-179.8503
	D6	D(3,1,5,8)	60.0173
	D7	D(4,1,5,6)	59.8719
D8	D(4,1,5,7)	-59.8548	
D9	D(4,1,5,8)	-179.9872	
D10	D(1,5,8,9)	-179.9213	
D11	D(6,5,8,9)	-59.4619	
D12	D(7,5,8,9)	59.6254	
D13	D(5,8,9,10)	-179.9973	
D14	D(5,8,9,11)	0.0156	
D15	D(8,9,11,12)	-179.9103	
D16	D(8,9,11,13)	60.0758	
D17	D(8,9,11,14)	-59.8665	
D18	D(10,9,11,12)	0.1033	
D19	D(10,9,11,13)	-119.9105	
D20	D(10,9,11,14)	120.1471	

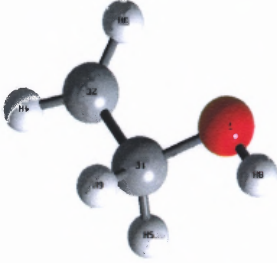
B.1.14 CCOC(O)C ₃					
			R1	R(1,2)	1.0931
			R2	R(1,3)	1.0931
			R3	R(1,4)	1.0944
			R4	R(1,5)	1.5182
			R5	R(5,6)	1.097
			R6	R(5,7)	1.097
			R7	R(5,8)	1.4379
			R8	R(8,9)	1.3619
			R9	R(9,10)	1.2068
			R10	R(9,11)	1.5166
			R11	R(11,12)	1.0889
			R12	R(11,13)	1.0946
			R13	R(11,14)	1.0946
D1	D(2,1,5,6)	179.866	A1	A(2,1,3)	108.336
D2	D(2,1,5,7)	60.1394	A2	A(2,1,4)	108.6009
D3	D(2,1,5,8)	-59.9931	A3	A(2,1,5)	110.5903
D4	D(3,1,5,6)	-60.1236	A4	A(3,1,4)	108.6005
D5	D(3,1,5,7)	-179.8503	A5	A(3,1,5)	110.5933
D6	D(3,1,5,8)	60.0173	A6	A(4,1,5)	110.0579
D7	D(4,1,5,6)	59.8719	A7	A(1,5,6)	110.6426
D8	D(4,1,5,7)	-59.8548	A8	A(1,5,7)	110.6403
D9	D(4,1,5,8)	-179.9872	A9	A(1,5,8)	107.234
D10	D(1,5,8,9)	-179.9213	A10	A(6,5,7)	108.0576
D11	D(6,5,8,9)	-59.4619	A11	A(6,5,8)	110.1419
D12	D(7,5,8,9)	59.6254	A12	A(7,5,8)	110.136
D13	D(5,8,9,10)	-179.9973	A13	A(5,8,9)	121.8721
D14	D(5,8,9,11)	0.0156	A14	A(8,9,10)	118.6598
D15	D(8,9,11,12)	-179.9103	A15	A(8,9,11)	117.9832
D16	D(8,9,11,13)	60.0758	A16	A(10,9,11)	123.3571
D17	D(8,9,11,14)	-59.8665	A17	A(9,11,12)	107.9906
D18	D(10,9,11,12)	0.1033	A18	A(9,11,13)	111.3641
D19	D(10,9,11,13)	-119.9105	A19	A(9,11,14)	111.3906
D20	D(10,9,11,14)	120.1471	A20	A(12,11,13)	109.3018
			A21	A(12,11,14)	109.3133
			A22	A(13,11,14)	107.4542

B.1.15 CCCN					
			R1	R(2,1)	1.5309
			R2	R(3,2)	1.5297
			R3	R(4,3)	1.4672
			R4	R(5,1)	1.0945
			R5	R(6,1)	1.0959
			R6	R(7,1)	1.0961
			R7	R(8,2)	1.096
			R8	R(9,2)	1.0995
			R9	R(10,3)	1.1062
			R10	R(11,3)	1.0978
			R11	R(12,4)	1.0174
			R12	R(13,4)	1.0184
D1	D(3,2,1,5)	-179.5088	A1	A(1,2,3)	113.0606
D2	D(3,2,1,6)	60.5385	A2	A(2,3,4)	110.7348
D3	D(3,2,1,7)	-59.4053	A3	A(2,1,5)	111.3187
D4	D(8,2,1,5)	58.8329	A4	A(2,1,6)	111.2329
D5	D(8,2,1,6)	-61.1198	A5	A(5,1,6)	107.5706
D6	D(8,2,1,7)	-181.0636	A6	A(2,1,7)	111.4266
D7	D(9,2,1,5)	-57.8452	A7	A(5,1,7)	107.5861
D8	D(9,2,1,6)	-177.7979	A8	A(6,1,7)	107.5062
D9	D(9,2,1,7)	62.2582	A9	A(1,2,8)	110.5055
D10	D(4,3,2,1)	-178.1016	A10	A(3,2,8)	108.3668
D11	D(4,3,2,8)	-55.2474	A11	A(1,2,9)	109.457
D12	D(4,3,2,9)	59.9562	A12	A(3,2,9)	108.961
D13	D(10,3,2,1)	55.7602	A13	A(8,2,9)	106.2501
D14	D(10,3,2,8)	-181.3856	A14	A(2,3,10)	108.8937
D15	D(10,3,2,9)	-66.182	A15	A(4,3,10)	114.0276
D16	D(11,3,2,1)	-59.7849	A16	A(2,3,11)	109.0645
D17	D(11,3,2,8)	63.0693	A17	A(4,3,11)	107.6768
D18	D(11,3,2,9)	-181.7272	A18	A(10,3,11)	106.2508
D19	D(12,4,3,2)	-182.4309	A19	A(3,4,12)	109.9094
D20	D(12,4,3,10)	-59.211	A20	A(3,4,13)	109.4359
D21	D(12,4,3,11)	58.412	A21	A(12,4,13)	105.8871
D22	D(13,4,3,2)	-66.5479			
D23	D(13,4,3,10)	56.672			
D24	D(13,4,3,11)	-185.705			

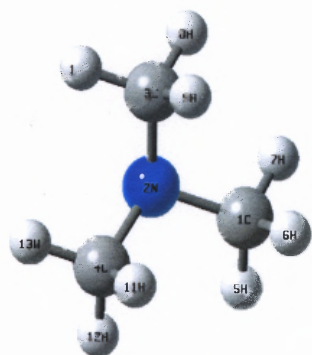
B.1.16 CCOH		
R1	R(1,2)	1.5194
R2	R(1,6)	1.1023
R3	R(1,7)	1.1023
R4	R(1,8)	1.4237
R5	R(2,3)	1.0939
R6	R(2,4)	1.0946
R7	R(2,5)	1.0939
R8	R(8,9)	0.9656
A1	A(2,1,6)	109.815
A2	A(2,1,7)	109.8112
A3	A(2,1,8)	107.8749
A4	A(6,1,7)	107.0707
A5	A(6,1,8)	111.1343
A6	A(7,1,8)	111.1388
A7	A(1,2,3)	110.3978
A8	A(1,2,4)	110.6374
A9	A(1,2,5)	110.4139
A10	A(3,2,4)	108.5772
A11	A(3,2,5)	108.166
A12	A(4,2,5)	108.5777
A13	A(1,8,9)	108.0122
D1	D(6,1,2,3)	179.0181
D2	D(6,1,2,4)	58.8029
D3	D(6,1,2,5)	-61.4234
D4	D(7,1,2,3)	61.5369
D5	D(7,1,2,4)	-58.6783
D6	D(7,1,2,5)	-178.9046
D7	D(8,1,2,3)	-59.7241
D8	D(8,1,2,4)	-179.9393
D9	D(8,1,2,5)	59.8344
D10	D(2,1,8,9)	-179.9998
D11	D(6,1,8,9)	-59.5669
D12	D(7,1,8,9)	59.5692

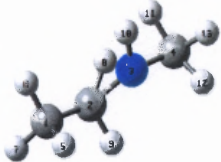


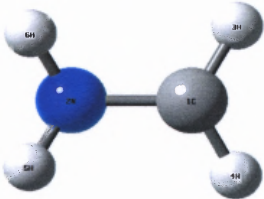
B.1.17 C ₂ COH		
R1	R(1,2)	1.4832
R2	R(1,5)	1.1089
R3	R(1,6)	1.1091
R4	R(1,7)	1.4217
R5	R(2,3)	1.0828
R6	R(2,4)	1.0837
R7	R(7,8)	0.9652
A1	A(2,1,5)	110.0348
A2	A(2,1,6)	110.0312
A3	A(2,1,7)	109.0621
A4	A(5,1,6)	105.3308
A5	A(5,1,7)	111.1788
A6	A(6,1,7)	111.161
A7	A(1,2,3)	119.8615
A8	A(1,2,4)	120.2698
A9	A(3,2,4)	119.8668
A10	A(1,7,8)	107.9054
D1	D(5,1,2,3)	-122.6082
D2	D(5,1,2,4)	57.8882
D3	D(6,1,2,3)	121.766
D4	D(6,1,2,4)	-57.7377
D5	D(7,1,2,3)	-0.4089
D6	D(7,1,2,4)	-179.9125
D7	D(2,1,7,8)	-179.4589
D8	D(5,1,7,8)	-57.9519
D9	D(6,1,7,8)	59.0502



B.1.18 C ₂ NC					
			R1	R(2,1)	1.4552
			R2	R(3,2)	1.4552
			R3	R(4,2)	1.4551
			R4	R(5,1)	1.0949
			R5	R(6,1)	1.1084
			R6	R(7,1)	1.0949
			R7	R(8,3)	1.0949
			R8	R(9,3)	1.1084
			R9	R(10,3)	1.0949
			R10	R(11,4)	1.1084
			R11	R(12,4)	1.0948
			R12	R(13,4)	1.0948
			A1	A(1,2,3)	111.5318
			A2	A(1,2,4)	111.5486
			A3	A(3,2,4)	111.5316
D1	D(3,2,1,5)	-176.6614	A4	A(2,1,5)	109.794
D2	D(3,2,1,6)	62.6285	A5	A(2,1,6)	113.3632
D3	D(3,2,1,7)	-58.0768	A6	A(5,1,6)	107.8684
D4	D(4,2,1,5)	57.888	A7	A(2,1,7)	109.7975
D5	D(4,2,1,6)	-62.8222	A8	A(5,1,7)	107.9919
D6	D(4,2,1,7)	176.4725	A9	A(6,1,7)	107.8627
D7	D(8,3,2,1)	57.8382	A10	A(2,3,8)	109.8017
D8	D(8,3,2,4)	183.2983	A11	A(2,3,9)	113.3526
D9	D(9,3,2,1)	-62.8668	A12	A(8,3,9)	107.8657
D10	D(9,3,2,4)	62.5933	A13	A(2,3,10)	109.799
D11	D(10,3,2,1)	176.4328	A14	A(8,3,10)	107.9956
D12	D(10,3,2,4)	-58.1071	A15	A(9,3,10)	107.8636
D13	D(11,4,2,1)	62.7113	A16	A(2,4,11)	113.3633
D14	D(11,4,2,3)	-62.7395	A17	A(2,4,12)	109.7769
D15	D(12,4,2,1)	-57.9987	A18	A(11,4,12)	107.8779
D16	D(12,4,2,3)	176.5505	A19	A(2,4,13)	109.7924
D17	D(13,4,2,1)	-176.5823	A20	A(11,4,13)	107.8664
D18	D(13,4,2,3)	57.9669	A21	A(12,4,13)	108.002



B.1.19 CCNC					
			R1	R(2,1)	1.5263
			R2	R(3,2)	1.4602
			R3	R(4,3)	1.4573
			R4	R(5,1)	1.0944
			R5	R(6,1)	1.0967
			R6	R(7,1)	1.0938
			R7	R(8,2)	1.1083
			R8	R(9,2)	1.0983
			R9	R(10,3)	1.018
			R10	R(11,4)	1.1062
			R11	R(12,4)	1.0962
			R12	R(13,4)	1.0942
			A1	A(1,2,3)	111.1325
			A2	A(2,3,4)	113.2346
			A3	A(2,1,5)	110.9566
			A4	A(2,1,6)	111.1119
			A5	A(5,1,6)	107.5161
			A6	A(2,1,7)	110.5529
			A7	A(5,1,7)	108.6794
			A8	A(6,1,7)	107.9045
			A9	A(1,2,8)	109.6407
A10	A(3,2,8)	112.7144			
A11	A(1,2,9)	109.5697			
A12	A(3,2,9)	107.5947			
A13	A(8,2,9)	106.0076			
A14	A(2,3,10)	108.7701			
A15	A(4,3,10)	109.1416			
A16	A(3,4,11)	114.5104			
A17	A(3,4,12)	109.4291			
A18	A(11,4,12)	107.2961			
A19	A(3,4,13)	109.7088			
A20	A(11,4,13)	108.1213			
A21	A(12,4,13)	107.5297			
D1	D(3,2,1,5)	-177.6926			
D2	D(3,2,1,6)	62.7458			
D3	D(3,2,1,7)	-57.0374			
D4	D(8,2,1,5)	57.0328			
D5	D(8,2,1,6)	-62.5287			
D6	D(8,2,1,7)	-182.3119			
D7	D(9,2,1,5)	-58.9192			
D8	D(9,2,1,6)	-178.4807			
D9	D(9,2,1,7)	61.7361			
D10	D(4,3,2,1)	-178.291			
D11	D(4,3,2,8)	-54.7557			
D12	D(4,3,2,9)	61.7553			
D13	D(10,3,2,1)	-56.7714			
D14	D(10,3,2,8)	66.7639			
D15	D(10,3,2,9)	-176.7251			
D16	D(11,4,3,2)	54.5318			
D17	D(11,4,3,10)	-66.7789			
D18	D(12,4,3,2)	-65.953			

B.1.20 CH _{2j} NH ₂					
			R1	R(1,2)	1.4
			R2	R(1,3)	1.0852
			R3	R(1,4)	1.0853
			R4	R(2,5)	1.0133
			R5	R(2,6)	1.0133
			A1	A(2,1,3)	115.8676
			A2	A(2,1,4)	115.8689
			A3	A(3,1,4)	117.5824
			A4	A(1,2,5)	114.3692
			A5	A(1,2,6)	114.3666
			A6	A(5,2,6)	110.1226
			D1	D(3,1,2,5)	-172.2246
			D2	D(3,1,2,6)	-43.9253
			D3	D(4,1,2,5)	43.9709
			D4	D(4,1,2,6)	172.2703

B.2 SMCPS Input Files

B.2.1 CCNCO₂CC

NAME (name of molecule)
ccnco2cc

COMMENTS:
from ccnco2cc.log in e: b3lyp/6-31g(d,p)

TEMPERATURE
8 (Number of temperature to be read in)
298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR
0 number of internal rotors

MOLECULAR WT
117

OPTICAL ISOMER
1

MULTIPLICITY
1 multiplicity of molecular specie of interest

HF298
-97.88

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 5 H 11 O 2 N 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)
1 (integer input)

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

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²
2 choice of moment of inertia units
3.7307403 1.1663177 1.0131828

SYMMETRY
9

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

51

50.2224	58.7010	99.1544
112.0284	192.3233	232.5263
278.1109	342.0112	403.0525
435.2945	494.7764	570.2607
643.6679	762.9891	787.6765
802.7768	855.6768	916.6205
958.8640	1061.1696	1097.4753
1119.3678	1137.7212	1187.9672
1203.7816	1321.2966	1337.8272
1355.8204	1399.8841	1419.6534
1424.5637	1442.7045	1476.4530
1498.2408	1500.8237	1505.6853
1509.7267	1520.0821	1524.3823
1821.2800	3046.0922	3052.7393
3063.9767	3080.7777	3111.6181
3121.0607	3125.9483	3132.7093
3138.9136	3151.9398	3654.1264

B.2.2 CCCNCO₂C

NAME (name of molecule)
CCCNCO2C

COMMENTS:
from cccnco2c.log in e: b3lyp/6-31g(d,p)

TEMPERATURE
8 (Number of temperature to be read in)
298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR
0 number of internal rotors

MOLECULAR WT
117

OPTICAL ISOMER
1

MULTIPLICITY
1 multiplicity of molecular specie of interest

HF298
-101.07

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 5 H 11 O 2 N 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)
1 (integer input)

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

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²
2 choice of moment of inertia units
3.8436449 1.0489492 0.8919668

SYMMETRY
9

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

51

51.3973	69.3662	91.2844
109.2211	161.9278	225.7191
249.4676	281.0384	335.0561
403.5193	492.8596	612.3921
651.5690	757.3371	764.0882
860.6733	893.6995	899.9634
1039.1495	1067.6868	1125.0117
1139.2155	1182.6086	1191.4285
1214.5649	1281.5889	1327.8839
1343.0813	1378.0125	1425.4856
1428.3450	1475.5786	1486.7751
1495.0604	1505.8698	1509.3116
1515.3523	1519.4893	1523.8187
1829.3510	3037.7700	3039.5512
3052.0028	3062.3447	3079.5344
3106.2509	3118.3901	3121.5125
3139.1812	3166.1787	3656.7413

B.2.3 CCN_jCO₂CC

NAME (name of molecule)

CCNjCO2CC

COMMENTS:

from CCjNCO2CC.log in e: b3lyp/6-31g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

116

OPTICAL ISOMER

1

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

-51.85

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 5 H 10 O 2 N 1

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

5.2949706 1.0136952 0.9552654

SYMMETRY

9

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

48

32.7330	48.0462	78.5879
109.2843	195.2498	225.1812
279.2199	334.9451	371.4523
399.9413	503.5988	615.3151
768.5950	804.0593	833.8490
875.4547	886.6299	951.8971
1003.5893	1053.9390	1119.3354
1131.3945	1179.3426	1207.3519
1278.9391	1300.5217	1336.7134
1351.8347	1408.9496	1411.6024
1433.7221	1498.4422	1502.0389
1503.0492	1508.4750	1521.8433
1526.6984	1711.3390	3033.9744
3055.8270	3056.0508	3082.3912
3094.3298	3126.7173	3132.9739
3134.8411	3142.6695	3154.5344

B.2.4 CC_jNCO₂CC

NAME (name of molecule)
CCjNCO2CC

COMMENTS:

from CCjNCO2CC.log in e: b3lyp/6-31g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)
298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

116

OPTICAL ISOMER

1

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

-63.51

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 5 H 10 O 2 N 1

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

3.2386413 1.3861900 1.0598035

SYMMETRY

9

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

48

45.3191	70.1183	101.7909
143.1370	177.3860	216.8796
240.7396	321.5121	350.2052
396.0179	441.1887	587.1255
612.0782	707.1793	733.1757
791.2179	862.2162	920.9538
975.0497	1019.0850	1072.5180
1118.3371	1132.4832	1201.1000
1235.0822	1337.2003	1377.4657
1408.2647	1423.0138	1444.6644
1455.2882	1482.7749	1494.1024
1500.1009	1505.1504	1512.3223
1523.5299	1803.8965	2990.4710
3053.9600	3076.8572	3084.1939
3123.0725	3125.3926	3134.9682
3153.8687	3220.9181	3637.2064

B.2.5 C_jCNCO₂CC

NAME (name of molecule)

CjCNCO2CC

COMMENTS:

from CjCNCO2CC.log in e: b3lyp/6-31g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

116

OPTICAL ISOMER

1

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

-54.39

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 5 H 10 O 2 N 1

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

4.5456294 1.0487746 0.9237799

SYMMETRY

6

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

48

37.6727	64.6937	105.1806
122.6338	171.1280	215.7337
242.2293	337.1419	360.3668
436.2090	492.4680	520.1904
555.3991	675.0992	760.7053
788.6091	836.1672	869.5720
959.2937	1026.8398	1087.1191
1110.7533	1127.5839	1148.0005
1200.1942	1249.2066	1336.8893
1350.8435	1387.5910	1417.8994
1442.4931	1468.7358	1473.4326
1497.4807	1499.1960	1504.1962
1523.6334	1820.7411	2990.4317
3029.0286	3053.1596	3081.3868
3121.0986	3134.1516	3153.4546
3167.2024	3278.5672	3652.5201

B.2.6 CCNCO₂C_jC

NAME (name of molecule)

CCNCO2CjC

COMMENTS:

from CCNCO2CjC.log in e: b3lyp/6-31g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

116

OPTICAL ISOMER

1

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

-48.49

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 5 H 10 O 2 N 1

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

3.4923328 1.2514025 1.0615856

SYMMETRY

9

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

48

44.9246	57.1557	94.8283
116.0966	184.9268	212.7500
250.2884	298.1885	406.9788
417.6578	491.7220	518.7234
575.2461	671.3861	746.0662
801.2375	827.8670	921.3964
958.8906	1024.2331	1076.2958
1113.8087	1141.7311	1191.4458
1238.8813	1317.9649	1347.5430
1386.7619	1418.0678	1426.0283
1430.5417	1475.2796	1478.9472
1503.3653	1507.9803	1509.8048
1520.1058	1835.8173	2974.6077
3047.2068	3065.9633	3093.3244
3113.5802	3126.4513	3139.5160
3143.6767	3203.0483	3656.6272

B.2.7 CCNCO₂CC_j

NAME (name of molecule)

CCNCO2CCj

COMMENTS:

from CCNCO2CCj.log in e: b3lyp/6-31g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

116

OPTICAL ISOMER

1

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

-57.49

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 5 H 10 O 2 N 1

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

2.9496749 1.3206689 0.9983932

SYMMETRY

6

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

48

32.2584	56.5813	83.6214
130.4123	159.1335	176.7316
238.1969	314.2565	383.0927
415.4129	463.0899	489.8138
584.5452	631.0005	761.6994
798.6787	823.5520	906.4462
957.2404	1003.7380	1078.3188
1105.0247	1130.8834	1136.8062
1191.4103	1240.8885	1318.4953
1350.2551	1391.1437	1422.3630
1434.6540	1466.9749	1477.0991
1497.5738	1506.2854	1511.8137
1521.5559	1823.8085	2988.8630
3046.3773	3048.9747	3065.0413
3111.3851	3125.4952	3138.9334
3176.8071	3287.3745	3655.1161

B.2.8 CCCN_jCO₂C

NAME (name of molecule)

CCCN_jCO₂C

COMMENTS:

from CCCN_jCO₂C.log in e: b3lyp/6-31g(d,p)

TEMPERATURE

8 (Number of temperature to be read in)

298 300 400 500 600 800 1000 1500 (Values of temperature to be read)

ROTOR

0 number of internal rotors

MOLECULAR WT

116

OPTICAL ISOMER

1

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

-55.7

STOICHIOMETRY (in form of "atom x" "number of atom x")

C 5 H 10 O 2 N 1

(do not put any comments on same line as stoichiometry info)

(The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)

1 (integer input)

!rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib)

!0.8 1.2 1.1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²

2 choice of moment of inertia units

4.8839553 0.9170984 0.8797683

SYMMETRY

9

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

48

31.0761	49.4322	80.3667
122.3195	156.5003	235.1216
244.6315	281.7974	315.7766
400.3319	494.3874	630.0074
764.8610	780.2246	871.8389
889.5932	920.1371	1003.3535
1030.2056	1078.7947	1143.0052
1177.6181	1178.7370	1219.2967
1268.8362	1300.4888	1313.9593
1336.4530	1365.1452	1425.2842
1480.5280	1496.1503	1505.7909
1510.0279	1511.0927	1514.4562
1528.1654	1715.5166	3025.7690
3044.7953	3051.5864	3063.3667
3080.0205	3096.3698	3119.9131
3121.2142	3140.1994	3175.9830

B.2.9 CCCjNCO₂C

NAME (name of molecule)
 CCCjNCO2C

COMMENTS:
 from CCCjNCO2C.log in e: b3lyp/6-31g(d,p)

TEMPERATURE
 8 (Number of temperature to be read in)
 298 300 400 500 600 800 1000 1500 (Values of temperature to be
 read)

ROTOR
 0 number of internal rotors

MOLECULAR WT
 116

OPTICAL ISOMER
 1

MULTIPLICITY
 2 multiplicity of molecular specie of interest

HF298
 -60.45

STOICHIOMETRY (in form of "atom x" "number of atom x")
 C 5 H 10 O 2 N 1
 (do not put any comments on same line as stoichiometry info)
 (The stoichiometry is NOT sorted. Will write to *.lst file as is).

RSCALING FACTOR (Uses Scott & Radom's scaling factors)
 1 (integer input)

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

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²
 2 choice of moment of inertia units
 3.9352476 1.1262856 0.8929850

SYMMETRY
 9

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)

48

43.7829	59.6548	104.8896
132.9336	151.3763	202.7517
242.3463	260.2892	323.2661
368.3054	399.8458	607.8644
622.9686	723.5789	734.1191
788.7432	866.9160	915.8722
1037.4273	1077.0338	1082.3598
1139.8941	1182.2288	1213.7957
1236.6831	1273.6089	1321.3575
1407.5435	1424.8149	1457.2483
1481.7063	1492.7542	1495.1892
1506.5150	1511.5557	1516.8841
1523.1245	1811.8303	2970.4526
3044.0643	3056.9273	3064.6414
3111.4872	3123.3528	3142.5119
3170.6074	3204.6519	3637.0333

REFERENCES

SECTION I

1. Denisov, E. T., *Polymer Degradation and Stability* **49** (1995) 71-75.
2. Denisov, E. T., *Russian J. Phys. Chem.*, **67** (1993) 2416.
3. Denisov, E. T., *Kinet. Catal.* (English translation), **32** (1991) 406.
4. Denisov, E. T., *Mendeleev. Commun.*, **2** (1992) 1.
5. Denisov, E. T. & Drozdova T. I., *Kinet. Catal.* (English translation), **35** (1994) 155.
6. Tsang, W.; Hampson, R. F., *J. Phys. Chem. Ref. Data* **15**, **1986**, 1087.
7. Tsang, W., *J. Phys. Chem. Ref. Data*, **17**, **1988**, 887.
8. Tsang, W., *J. Phys. Chem. Ref. Data*, **19**, **1990**, 1.00-68.00.
9. Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A., *J. Chem. Phys.* **110**, 4703 (1999).
10. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
11. Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A., *J. Chem. Phys.* **109**, 7764 (1998).
12. Curtiss, L. A.; Raghavachari, K.; Pople, J. A., *J. Chem. Phys.* **1998**, 1293 (1993).
13. Becke, A. D., *J. Chem. Phys.* **1998**, 5648 (1993).
14. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., *J. Phys. Chem.* **1998**, 11623 (1994).

15. Durant, J. L. Rohlffing, C. M. *J. Chem. Phys.* **1993**, 98, 8031.
16. Petersson, G. A.; Malick, D. K.; Wilson, W. G. *J. Chem. Phys.* **1998**, 109, 10570.
17. Scott, A.P.; Radom, L. *J. Phys. Chem.* **1996**, 100, 16502.
18. Hehre, W.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab-Initio Molecular Orbital Theory*; Wiley & Sons: New York, **1986**.
19. Stewart, J. J. P., *MOPAC 6.0*, Frank J. Seiler Research Lab., US Air Force Academy: Colorado, 1990.
20. Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* **1942**, 10, 428.
21. (a) Pitzer, K. S. *J. Chem. Phys.* **1937**, 5, 469, (b) *ibid.* **1946**, 14, 239.
22. Kilpatrick, J. E.; Pitzer, K. S. *J. Chem Phys.* **1949**, 11, 1064.
23. Ritter, E. R. and Bozzelli, J. W., *Int. J. Chem. Kinet.* **1991**, 23, 767.
24. Kee, R. J., Miller, J. A. and Jefferson, T. H., 'CHEMKIN: Fortran Chemical Kinetics Code Package', Sandia Report, SAND80-8003. UC-4(1980).
25. (a) McBride, B. J. and Gorden, S., 'Fortran IV Program for Calculation of Thermodynamic Data', NASA Report TN-D 4097.
(b) McBride, B. J., 'Computer Program for Calculating and Fitting Thermodynamic Functions', NASA Report RP 1271.
26. Steinfield, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: New York, 1989.
27. Chase, M. W., Jr., NIST-JANAF Thermochemical Tables, Fourth Edition, *J. Phys. Chem. Ref. Data*, Monograph 9, **1998**, 1-1951.
28. Ruscic, B.; Litorja, M., *J. Electron Spectroscopy and Related Phenomena.* 97, 1998, 131-146.
29. Pittam, D. A.; Pilcher, G., Measurements of heats of combustion by flame calorimetry Part 8.-Methane, ethane, propane, n-butane and 2-methylpropane, *J. Chem. Soc. Faraday Trans. 1*, **1972**, 68, 2224-2229.
30. Tsang, W.; Heats of Formation of Organic Free Radicals by Kinetic Methods in *Energetics of Organic Free Radicals*, Martinho Simoes, J. A.; Greenberg, A.; Liebman, J. F., eds., Blackie Academic and Professional, London, **1996**, 22-58.

31. THERM²³
32. Prosen, E. J.; Maron, F. W.; Rossini, F. D., Heats of combustion, formation, and isomerization of ten C₄ hydrocarbons, *J. Res. NBS*, **1951**, 46, 106-112.
33. Pilcher, G.; Chadwick, J.D.M., Measurements of heats of combustion by flame calorimetry. Part 4.-n-Pentane, isopentane, neopentane, *Trans. Faraday Soc.*, **1967**, 63, 2357-2361.
34. Sheng, C. Ph. D. Dissertation, Dept. Of Chemical Engineering, NJIT, 2002.
35. Chen, C. and Bozzelli, J. W., *J. Phys. Chem. A* **2002**, 104, 4997-5012.
36. Zhu, L.; Bozzelli, J. W. *Chem. Phys. Lett.* **2002**, 357, 65.

SECTION II

1. Stewart, J. J. P. *MOPAC 6.0*; Frank J. Seiler Research Lab., U.S. Air Force Academy: Colorado, 1990.
2. Petersson, G. A.; Malick, D. K.; Wilson, W. G. *J. Chem Phys.* **1998**, 109, 10570.
3. Mayer, P. M.; Parkinson, O. J.; Smith, D. M.; Radom, L, *J. Chem. Phys.* **1998**, 108, 604.
4. Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Chem. Phys.* **1998**, 102, 9965.
5. Wong, M. W.; Radom, L, *J. Chem. Phys, A* **1998**, 102, 2237.
6. Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A, *J. Chem. Phys* **1996**, 104, 2598.
7. Yamada, T.; Lay, T. H.; Bozzelli, J. W. *J. Phys. Chem.* **1998**, 102, 7286.
8. Hehre, W.; Radom, L.; Schleyer, P. R. Pople, J. A. *Ab-Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.
9. Yamada, T.; Lay, T. H.; Bozzelli, J. W. *J. Phys. Chem.* **1999**, 103, 5602.
10. Benson, S. W., *Thermochemical Kinetics*. 2nd ed; Wiley-Inter-science: New York, 1976.
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian 94* (Gaussian, Inc., Pittsburgh, PA, 1995).
12. Lee, C.; Yang, W.; Parr, R. E. *G. Phys. Rev.* **1988**, B41, 785.
13. Becke, A. D. *J. Chem. Phys.* 19993, **1998**, 1372.
14. Montgomery, J. A.; Ochterski, J. W.; Peterson, G. A., *J. Phys. Chem.* **1994**, 101, 5900.
15. Durant, J. L. *Chem. Phys. Lett.* **1996**, 26, 595.

16. Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.
17. Verevkin, S. P.; Beckhaus, H. D.; Ruchardt, C.; *Thermochim. Acta*, **1992**, *197*, 27-39.
18. Green, J. H. S., Revision of the values of the heats of formation of normal alcohols, *Chem. Ind. (London)*, **1960**, 1215-1216.
19. Wilberg, K. B.; Crocker, L. S.; Morgan, K. M., Thermochemical studies of carbonyl compounds. 5. Enthalpies of reduction of carbonyl groups, *J. Am. Chem. Soc.*, **1991**, *113*, 3447-3450.
20. Hongyan Sun and Joseph W. Bozzelli, *J. Phys. Chem. A* **2001**, *105*, 9543-9552.
21. Dean, A. M.; Bozzelli, J. W.; "Combustion of Nitrogen Chemistry"; Gas-Phase Combustion Chemistry, Gardiner, Jr., W.C. (Editor), Springer-Verlag, NY, 2000.
22. Ritter, E. R.; Bozzelli, J. W. *Int. J. Chem. Kinet.* **1991**, *23*, 767.
23. Pittam, D. A., Pilcher, G., Measurements of heats of combustion by flame calorimetry. Part 8.-Methane, ethane, propane, n-butane and 2-methylpropane, *J. Chem. Soc. Faraday Trans. 1*, **1972**, *68*, 2224-2229.
24. J.B. Pedley, R. D. Naylor, S. P. Kirby.; Thermochemical Data of Organic Compounds, 2nd Edition, 89-156.
25. Issoire, J.; and Long, C; *Etude de la thermodynamique chimique de la reaction de formation des methylamines*, *Bull. Soc. Chim. France*, **1960**, 2004-2012.
26. Scott, D. W., 1-Aminopropane, 2-aminopropane, and 2-methyl-2-aminopropane. Vibrational assignments, conformational analyses, and chemical thermodynamic properties, *J. Chem. Thermodyn.*, **1971**, *3*, 843-852.
27. R. J. Berry, A. L. Wilson, M. Schwartz., A computational study of bond dissociation enthalpies and hydrogen abstraction energy barriers in model urethanes, *J. Molecular Structure (Theochem)* **496 (2000)** 121-129.