Kinetics of HO2 abstraction of H atoms from hydrocarbons and thermochemical properties of urethane monomers and radicals

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ABSTRACT

KINETICS OF HO_2 ABSTRACTION OF H ATOMS FROM HYDROCARBONS AND THERMOCHEMICAL PROPERTIES OF URETHANE MONOMERS AND RADICALS

by
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SECTION I: Kinetics of HO_2 Abstraction of H Atoms From Hydrocarbons

Structures, internal rotational barriers and ideal gas thermochemical properties, $\Delta H_f^0{}_{298}$ for representative series of transition states for abstraction of H atoms from primary, secondary and tertiary hydrocarbons by the HO_2 radical, TC-HOOH (1), TCC-HOOH (2), TC_2C-HOOH (3), TC_3C-HOOH (4), TC_2CC-HOOH (5), TC_2CC-HOOHC (6) and TC_3CCC-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 $S^0{}_{298}$ and $C_p(T)$ values ($300 \leq T/K \leq 1500$) 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. $\Delta H^{\dagger 0}{}_{,TS}$ 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. $\Delta H^{\dagger 0}{}_{,TS}$ 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 ($\Delta H^0_{f(298)}$) and bond energies are determined for the molecules and radicals at the B3LYP/6-31 G(d,p) Density Functional Calculation Level. Entropy ($S^0_{(298)}$) and heat capacity $C_p(T)$ are determined from the above structures and vibration frequencies. Enthalpies of formation ($\Delta_f H^0_{(298)}$) are estimated using total energies including zero point vibrational energy (ZPVE), thermal contributions for each species and the calculated ΔH^0_{rxn} 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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by
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KINETICS OF HO_2 ABSTRACTION OF H ATOMS FROM HYDROCARBONS AND THERMOCHEMICAL PROPERTIES OF URETHANE MONOMERS AND RADICALS

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This thesis is dedicated to my beloved family

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SECTION I

KINETICS OF HO_2 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, HO_2, 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.

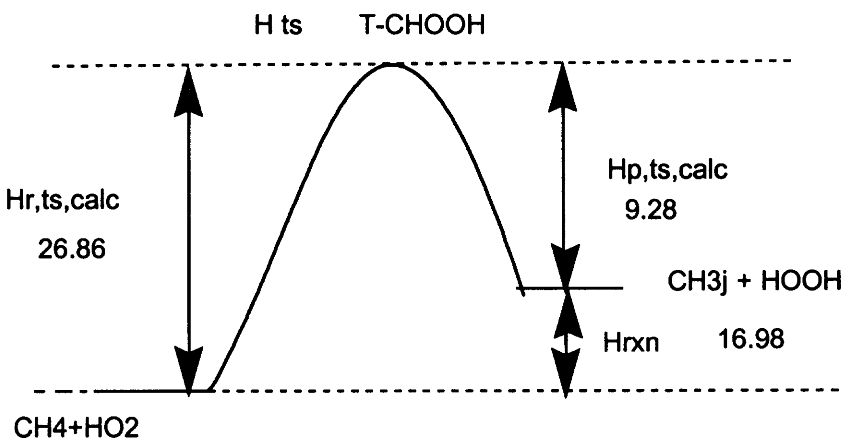


Figure 1.1 Pathway for CH_4 + HO_2 to CH_3 + HOOH. (Units in kcal/mol)

CHAPTER 2

LITERATURE SURVEY

Denisov[1], proposed an empirical method of estimation of bond dissociation energies[2]. 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 peroxyl radical with an inhibitor, such as phenol, amine or hydroxylamine is considered

$$RO_2^{\cdot} + InH \rightarrow ROOH + In^{\cdot} \qquad (2.1)$$

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

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

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

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

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 formula[4] (2.4)

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

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

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

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-cm^3/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 Expresssions 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)
$CH_4 + HO_2 \rightarrow CH_3 + HOOH$	1.81×10^{11} e-18.58/RT [6]
$C_2H_6 + HO_2 \rightarrow C_2H_5 + HOOH$	2.95×10^{11} e-14.94/RT [6]
$CCC + HO_2 \rightarrow CC_jC + HOOH$	2.61×10^{10} e-13.91/RT [7]
$C_3C + HO_2 \rightarrow C_3C_j + HOOH$	7.36×10^{9} $T^{2.55}$e-10.53/RT [8]
$C_3C + HO_2 \rightarrow C_{3j}C + HOOH$	6.14×10^{10} $T^{2.55}$e-15.5/RT [8]

CHAPTER 3

CALCULATION METHODS

G3(MP2)[9] method in Gaussian 98 program suite[10] is used for all calculations. G3(MP2) theory, is a modification of the G3 theory[11], which is much more accurate and requires less computational time and scratch space than the G2(MP2) theory[12]. Both the G3(MP2) and CBS-Q theories use the B3LYP density functional method[13,14] for geometries and zero-point energies. Durant[15] 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 al[17]. 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

$\Delta H_{f\,298}^{0}$ 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 ($\Delta H_{f\,298}^{0}$), 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, TC_2C-HOOH, TC_3C-HOOH and TC_2CC-HOOH. The initial structure of each compound or transition state is determined using UHF/PM3 in MOPAC[19], followed by optimization and vibrational frequency calculation at B3LYP/6-311 G(d,p) level of theory using Gaussian 98[10]. 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. $C_3C + HO_2 \rightarrow TC_2CC - HOOH \rightarrow C_{3j}C + HOOH$ Primary

6. $C_2CCC + HO_2 \rightarrow TC_2CC - HOOH - C \rightarrow C_2CC_jC + HOOH$ Secondary

The $\Delta H_f^0{}_{298}$'s of the transition state structures are estimated by evaluation of $\Delta H_f^0{}_{298}$ 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

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

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

$\Delta H\dagger^0{}_{,TS} = (\Delta H_{R,TS,calc} + \Delta H_{P,TS,calc}) / 2$

Calculation of H† for the transition state TC-HOOH is not taken as the calculated energy difference between reactant and transition state. The H† 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 $\Delta H_f^0{}_{298}$ of the reactants. $\Delta H_{P,TS,calc}$ is the difference between the calculated energy of the transition state and product plus $\Delta H_f^0{}_{298}$ of the products. $\Delta H\dagger^0{}_{,TS}$ 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 Gwinn[20] 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 Ix 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 **E**stimation for **R**adicals and **M**olecules) 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_jC 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 CHEMKIN[24] reaction modeling code or the NASA equilibrium code.[25] In addition, thermodynamic, kinetic and equlibrium 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 theory[26] (TST) for bi molecular reactions, $A_\infty = (ekT/h)\exp(\Delta S^{\ne}/R)$, 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 HO_2 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 HO_2 abstraction from CH_4, TC-HOOH, is 1.441A° as shown in Figure 4.1 and the forming H-O bond is 1.111 A°. The O-OH bond length also changed from 1.328 A° to 1.415 A°.

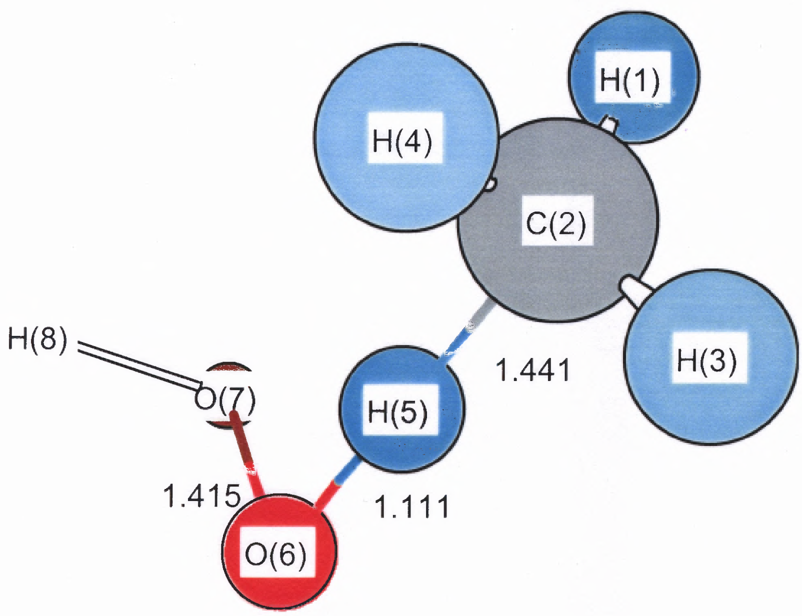


Figure 4.1 Geometry of the Transition State TC-HOOH (Units: Angstroms).

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 1.395A°, the forming H-O bond is 1.145 A° and the O-OH bond length is 1.415 A°. The cleaving C-H bond length in the transition state for the secondary carbon in propane, TC_2C-HOOH, is 1.364A°, the forming H-O bond is 1.171 A° and the O-OH bond length is 1.414 A°. The cleaving C-H bond length in the transition state for the tertiary C-H bond isobutene, TC_3C-HOOH, is 1.337A°, the forming H-O bond is 1.197 A° and the O-OH bond length is 1.413 A°. The cleaving C-H bond length in the transition state for the primary C-H bond in isobutene, TC_2CC-HOOH, is 1.395A°, the forming H-O bond is 1.146 A° and the O-OH bond length is 1.416 A°. The cleaving C-H bond length in the transition state for the secondary C-H bond in 2methylbutane, TC_2CC-HOOHC, is 1.367A°, the forming H-O bond is 1.174 A° and the O-OH bond length is 1.415 A°.

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, $\Delta H^0_{f\ 298}$ 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:

$$CH_4 + HO_2 \rightarrow TC - HOOH(TS1) \qquad \text{forward direction} \qquad (4.1)$$

$$CH_3 + HOOH \rightarrow TC - HOOH(TS1) \qquad \text{reverse direction} \qquad (4.2)$$

$\Delta H_{298\text{ to tst}} = \sum(\text{total energies})_{298}$ at saddle point tst - $\sum(\text{total energies})_{298}$ 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 CH_4 + HO_2 is 26.86 kcal/mol. The calculated $\Delta\Delta H_{f\ (298)}$ from the transtition state structure to the products H_2O_2 + 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 ΔH^0_{f298} 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 ΔH_{f298} 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 $\Delta H\dagger^{0}_{TS,298}$ 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 $\Delta H\dagger^{0}_{TS,298}$ 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. $\Delta H\dagger^{0}_{TS,298}$ 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_2H_6	-20.04±0.07[29]
C_2H_5	28.4±0.5[30]
CCC	-25.02±0.12[29]
CC_jC	22.0±0.5[30]
C_3C	-32.5[31]
C_3C	*-32.42 ± 0.13*[32]
C_3C_j	11.0[31]
C_3C_j	*11.0±0.7*[30]
$C_{3j}C$	*17.0±0.5*[30]
C_2CCC	-37.43[31]
C_2CCC	*-36.84 ± 0.23*[33]
C_2CC_jC	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_2H_6	0.074362	-79.781898	-79.777465	2.78	45.76	-79.77890732
C_2H_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_jC	0.087508	-118.42665	-118.420501	3.86	53.85	-118.4221989
C_3C	0.130993	-158.374895	-158.368241	4.18	80.60	-158.3707826
C_3C_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_2CCC	0.159361	-197.669262	-197.661268	5.02	98.06	-197.66436
C_2CC_jC	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 CCHOOH	0.084468	-230.689674	-230.682248	4.66	51.98	-230.6838868
T C_2C-HOOH	0.112792	-269.990793	-269.981949	5.55	69.41	-269.9841373
T C_3CHOOH	0.14071	-309.292425	-309.282142	6.45	86.58	-309.2848718
T $C_2CCHOOH$	0.141076	-309.283005	-309.273066	6.24	86.81	-309.2758031
T $C_2CCHOOHC$	0.169222	-348.582468	-348.57099	7.20	104.13	-348.5742734

[a]Optimized at the B3LYP/6-311G(d,p) level of theory, [b]ZPVE : Zero Point Correction in Hartree/Particle, [c]Sum of elec = Sum of electronic and zero-point energies in kcal/mol, [d]Sum of zpe = Sum of electronic and thermal enthalpies, [e]Thermal Corr: Thermal Corrections in Hartree, [f]scaled zero-point energies in kcal/mol (scaled by 0.9806), [g]B3LYP/6-311G(d,p). Total Energies are in Hartree at 0 K; Unit in Hartree = 627.51 kcal/mol. [h]T 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. $C_3C + HO_2 \rightarrow TC_2CCHOOH$ $C_{3j}C + HOOH \rightarrow TC_2CCHOOH$	27.32 12.37	16.59 2.35	13.27
6. $C_2CCC + HO_2 \rightarrow TC_2CCHOOHC$ $C_2CC_jC + HOOH \rightarrow TC_2CCHOOHC$	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)	$\Delta H\dagger^{0}{}_{,TS}$ (G3MP2)	$\Delta H\dagger^{0}{}_{,TS}$ (CBSQ)
1. TC-HOOH	11.87	6.67
2. TCC-HOOH	7.20	0.01
3. TC_2C-HOOH	1.23	-7.62
4. TC_3C-HOOH	-7.97	-18.65
5. TC_2CC-HOOH	-2.82	-13.20
6. TC_2CC-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 Gwinn[20], 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	$\Delta H_f^o{}_{298}$	$S^o{}_{298}$	$C_p{}^o$ (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_2H_6[f]	-20.20	54.81	12.52	15.73	18.64	21.26	25.71	29.21	34.71
C_2H_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_jC[f]	21.02	70.31	16.38	20.30	23.95	27.54	33.36	37.43	44.16
C_3C[f]	-32.5	70.43	23.11	29.52	35.37	40.42	48.37	54.36	63.92
C_3C_j[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_2CCC[f]	-37.43	82.03	28.61	36.47	43.62	49.77	59.44	66.70	78.12
C_2CC_jC[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
TCHOOH[b,c,d]	11.87	73.17	18.04	20.81	23.24	25.28	28.45	30.83	34.73
TCCHOOH[b,c,d]	7.20	83.78	22.38	26.71	30.56	33.81	38.91	42.72	48.76
TC_2CHOOH[b,c,d]	1.23	91.80	27.91	33.50	38.54	42.85	49.67	54.78	62.85
TC_3CHOOH[b,c,d]	-7.97	98.01	33.74	41.01	47.44	52.84	61.21	67.45	77.26
$TC_2CCHOOH$[b,c,d]	-2.82	100.7	33.28	40.93	47.57	53.05	61.45	67.62	77.33
$TC_2CCHOOHC$[b,c,d]	-9.07	107.6	38.79	47.72	55.55	62.08	72.19	79.67	91.42

a: $\Delta H_f^o{}_{298}$ in kcal/mol, $S^o{}_{298}$ and $C_p{}^o$ (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 THERM[23]

Table 4.6 Moments of Inertia (amu A^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_2CHOOH	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_3CHOOH	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_3C-HOOH	114.79	37.18	1.0^b	3
$TC_2CCHOOH$	C_2-CCHOOH	3.16	144.32	3.87^d	3
	C_2-CCHOOH	3.16	445.80	3.87^d	3
	C_2C-CHOOH	274.8	73.98	3.1^c	3
	C_2CC-HOOH	178.2	37.43	1.0^b	3
$TC_2CCHOOHC$	C_2-CCHOOHC	3.15	596.17	3.87^d	3
	C_2-CCHOOHC	3.15	667.11	3.87^d	3
	C_2C-CHOOHC	72.78	237.8	3.1^c	3
	C_2CCHOOH-C	3.15	421.04	2.8^c	3
	C_2CC-HOOHC	274.2	35.33	1.0^b	3

[a]Moments of inertia are computed from ROTATOR, [b]calculated using MMFF, [c]estimated value, [d]Reference 35 [e]n is the foldness. All calculations are at B3LYP/6-311G(d,p) level of calculation.

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

		$S^0{}_{298}$	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

[a]Pitzer and Gwinn[16] [b]ROTATOR

The barrier for RC-HOOH, which is 1.0, is calculated using Molecular Mechanics Force Field (MMFF) in Spartan. The $S^0{}_{298}$ and C_p(T) values of the stable molecules and product radicals are calculated from THERM[23]. 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 is this study.

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

The rate coefficients are expressed in the modified Arrhenius form:

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

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

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

Forward Reaction	A (cm^3/mol s)	n	Ea (G3MP2) (kcal/mol)	E_a (CBSQ) (kcal/mol)
k_1 $CH_4 + HO_2 \rightarrow$ T CHOOH	1.22×10^3	3.202	25.81	20.60
k_2 $C_2H_6 + HO_2 \rightarrow$ T CCHOOH	4.67×10^2	3.355	23.30	16.11
k_3 CCC + $HO_2 \rightarrow$ T C_2CHOOH	7.14×10^3	2.85	22.89	14.04
k_4 $C_3C + HO_2 \rightarrow$ T C_3CHOOH	3.18×10^3	3.007	20.82	10.14
k_5 $C_3C + HO_2 \rightarrow$ T C_2CCHOOH	6.86×10^3	3.084	25.89	15.51
k_6 C_2CCC + $HO_2 \rightarrow$ T C_2CCHOOHC	1.72×10^3	2.947	24.66	N/A

k_1, k_2, k_3, k_4, k_5, k_6 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	Ea (G3MP2) (kcal/mol)	E_a (CBSQ) (kcal/mol)
k_{-1} CH_3 + HOOH $\rightarrow$ T CHOOH	2.74×10^4	2.445	9.03	3.82
k_{-2} C_2H_5 + HOOH $\rightarrow$ T CCHOOH	2.88×10^2	2.954	10.46	3.27
k_{-3} CC_jC + HOOH $\rightarrow$ T C_2CHOOH	6.15×10^1	3.007	12.07	3.22
k_{-4} C_3C_j + HOOH $\rightarrow$ T C_3CHOOH	4.43×10^0	3.456	11.90	1.22
k_{-5} $C_{3j}C$ + HOOH $\rightarrow$ T C_2CCHOOH	4.41×10^2	2.843	12.63	2.24
k_{-6} C_2CC_jC + HOOH $\rightarrow$ T C_2CCHOOHC	2.90×10^1	3.103	13.85	N/A

k_{-1}, k_{-2}, k_{-3}, k_{-4}, k_{-5}, k_{-6} 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)

$$CH_4 + HO_2 \rightarrow T - CHOOH \rightarrow CH_3 + HOOH \quad \text{forward reaction} \qquad (4.4)$$

	CH_4 +	HO_2 →	TCHOOH
$\Delta H^{o}_{f\ 298}$ {kcal/mol}	-17.900	3.200	11.870
S^{o}_{298} {cal/mol K}	44.490	54.380	73.17

Aprime = 1.2160E+03   n = 3.20208   Ea = 2.5812E+04

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm3/mol s)	kcalc (cm3/mol s)	kfit (cm3/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

$$CH_3 + HOOH \rightarrow T - CHOOH \quad \text{reverse reaction} \qquad (4.5)$$

	CH_3 +	HOOH →	TCHOOH
$\Delta H^{o}_{f\ 298}$ {Kcal/mol}	-17.900	3.200	11.870
S^{o}_{298} {cal/mol K}	44.490	54.380	73.17

Aprime = 2.7443E+04   n = 2.44553   Ea = 9.0351E+03

Temp (K)	ΔH (kcal/mol)	ΔS (cal/mol K)	A' (cm3/mol s)	kcalc (cm3/mol s)	kfit (cm3/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:

$$\Delta G^0 = \Delta H^0 - T * \Delta S = -RT \ln K_{eq}$$

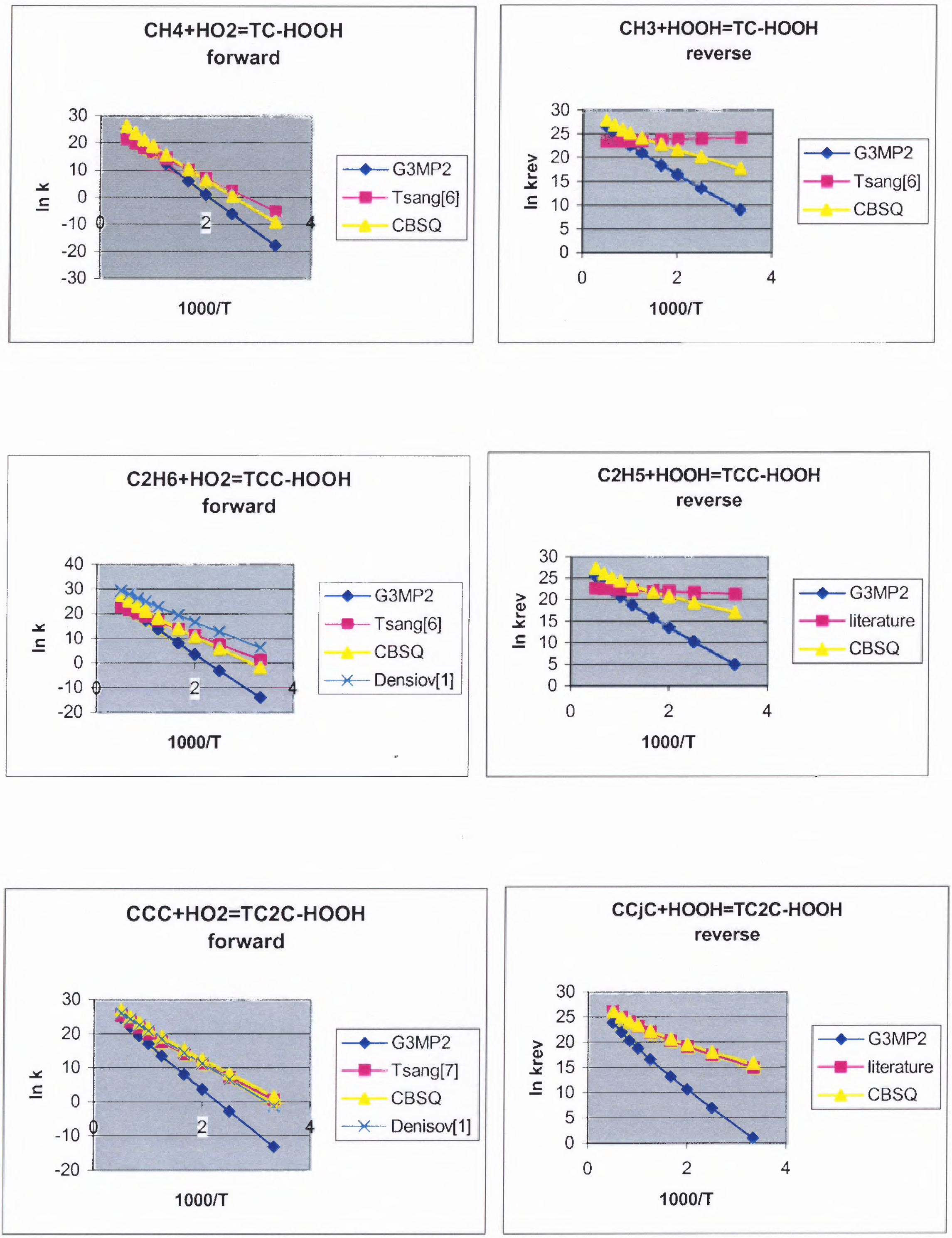
The K_{eq} values for the reactions are listed in Table 4.10

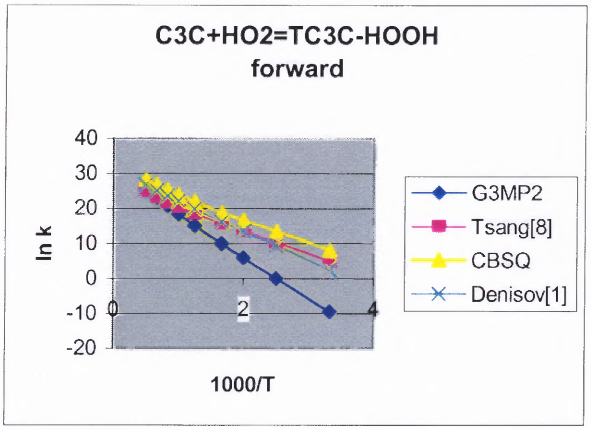
Table 4.10 Equilibrium Constants

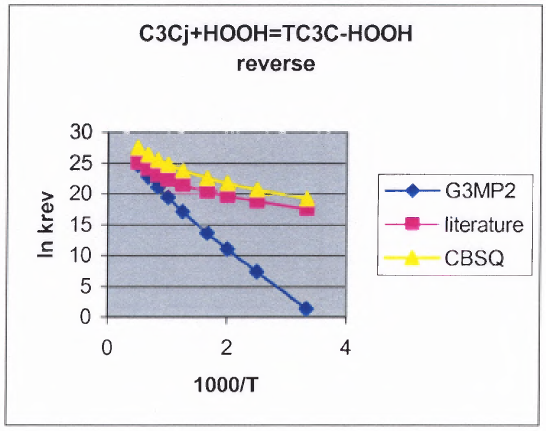
Reaction	K_{eq} at 300K
1. $CH_4 + HO_2 \rightarrow CH_3 + HOOH$	2.064E-12
2. $C_2H_6 + HO_2 \rightarrow C_2H_5 + HOOH$	7.205E-09
3. $CCC + HO_2 \rightarrow CC_jC + HOOH$	6.491E-07
4. $C_3C + HO_2 \rightarrow C_3C_j + HOOH$	1.795E-05
5. $C_3C + HO_2 \rightarrow C_{3j}C + HOOH$	1.365E-08
6. $C_2CCC + HO_2 \rightarrow C_2CC_jC + HOOH$	3.258E-07

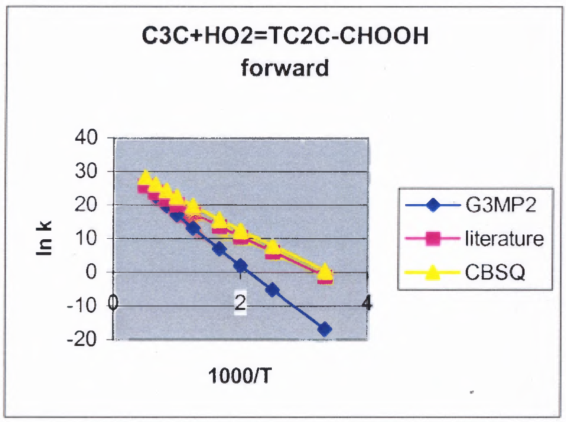
The forward and reverse rate constants are computed for some of the hydrogen abstraction reactions by the G3MP2 and CBSQ calculation methods and these values are compared with those available in literature (k_{lit}) as discussed in Table 2.2. Plots are made for ln(k) versus 1000/T where T is the temperature 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.

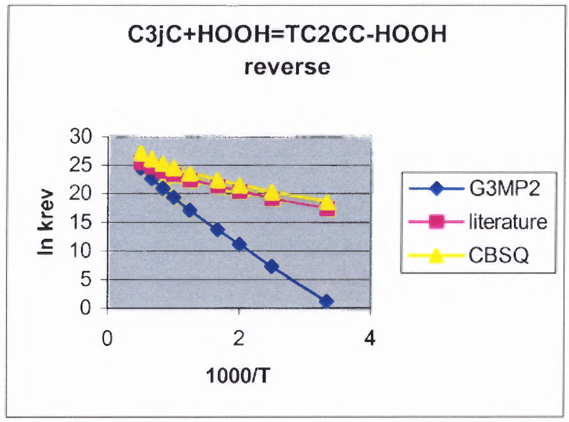
Figure 4.2 Plots of Rate Constants Calculated (k_{calc}) and From Literature (k_{lit}) vs T











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 cm^3/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 RH + HO_2 = R_o + HOOH systems using density functional calculations with enthalpies of formation ($\Delta H\dagger^{0}{}_{,TS}$) computed at the G3(MP2) level. Entropy ($S^o{}_{298}$) and heat capacity ($C_p{}^o$ (T)) (300 ≤ T/K≤ 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 $S^o{}_{298}$ and $C_p{}^o$ (T) for the transition states TCHOOH, TCCHOOH, TC_2CHOOH, TC_3CHOOH, $TC_2CCHOOH$ and $TC_2CCHOOHC$ 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, C_3-CHOOH 3.5, C_2-CCHOOH 3.87 and C_2C-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 $C_2CCHOOHC$.

The high-pressure limit rate constants are:

$k_{1,\infty}(CH_4 + HO_2 \rightarrow TCHOOH)$ = 1.22 x 10^3 $T^{3.202}$ exp(-25.81/RT) cm^3/mol-s;

$k_{2,\infty}(C_2H_6 + HO_2 \rightarrow TCCHOOH)$ = 4.67 x 10^2 $T^{3.355}$ exp(-23.30/RT) cm^3/mol-s;

$k_{3,\infty}(CCC + HO_2 \rightarrow TC_2CHOOH)$ = 7.14 x 10^3 $T^{2.85}$ exp(-22.89/RT) cm^3/mol-s;

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

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

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

Reverse rate constants are also reported:

$k_{-1,\infty}$= 2.74 x 10^4 $T^{2.445}$ exp(-9.03/*RT*) cm^3/mol-s; $k_{-2,\infty}$= 2.88 x 10^2 $T^{2.954}$ exp(-10.46/*RT*) cm^3/mol-s; $k_{-3,\infty}$= 6.15 x 10^1 $T^{3.007}$ exp(-12.07/*RT*) cm^3/mol-s; $k_{-4,\infty}$= 4.43 $T^{3.456}$exp(-11.9/*RT*) cm^3/mol-s; $k_{-5,\infty}$= 4.41 x 10^2 $T^{2.843}$ exp(-12.63/*RT*) cm^3/mol-s and $k_{-6,\infty}$= 2.90 x 10^1 $T^{3.103}$ exp(-13.85/*RT*) cm^3/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 MOPAC[1] and Density Functional Calculation methods.

CHAPTER 2

CALCULATION METHOD

The geometries of the reactants and product radicals are pre-optimized using UHF/PM3 in MOPAC[1]. 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 $\Delta H^0_{f(298)}$ 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 reactions[15]. 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)

- $CCNCO_2CC$

- $CCNjCO_2CC$
- $CCjNCO_2CC$
- $CjCNCO_2CC$
- $CCNCO_2CjC$
- $CCNCO_2CCj$
- $CCCNCO_2C$
- $CCCNjCO_2C$
- $CCCjNCO_2C$

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

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

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^0_{rxn} 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 $CCNCO_2CC$ 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 $CCCNCO_2C$, CCN_jCO_2CC, CC_jNCO_2CC, C_jCNCO_2CC, $CCNCO_2C_jC$, $CCNCO_2CC_j$, $CCCN_jCO_2C$, CCC_jNCO_2C, C_2NCCO_2C, CH_3NH_2, CH_3N_jH, $CH_{2j}NH_2$, CCOC(O)C, $CCOC(O)C_j$ and $CC_jOC(O)C$, CCOH, C_jCOH, C_2NC, 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.

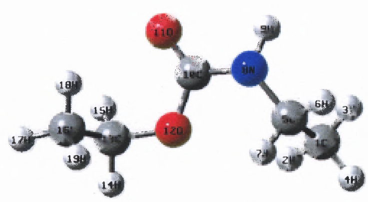


Figure 3.1 Structure of Ethyl N Ethyl Carbamate ($CCNCO_2CC$).

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)

CCNCO2CCj	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
CCCNjCO2C	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
CCCjNCO2C	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
$CCNCO_2CC$	3.7307403	1.1663177	1.0131828
$CCCNCO_2C$	3.8436449	1.0489492	0.8919668
$CCNjCO_2CC$	5.2949706	1.0136952	0.9552654
$CCjNCO_2CC$	3.2386413	1.3861900	1.0598035
CjCNCO2CC	4.5456294	1.0487746	0.9237799
$CCNCO_2CjC$	3.4923328	1.2514025	1.0615856
$CCNCO_2CCj$	2.9496749	1.3206689	0.9983932
$CCCNjCO_2C$	4.8839553	0.9170984	0.8797683
$CCCjNCO_2C$	3.9352476	1.1262856	0.8929850

[a]Optimized at the B3LYP/6-31G(d,p) level of theory. [b]Units in GHz.

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

The $\Delta H^0_{f(298)}$ values are calculated using the total energies and working isodesmic reactions. Enthalpies of formation $\Delta H^0_{f(298)}$ 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 $\Delta H^0_{f\,(298)}$ for Reference Species used in Reaction Schemes and Bond Energy Calculations

Species	$\Delta H^0_{f\,(298)}$ (kcal/mol)	Species	$\Delta H^0_{f\,(298)}$ (kcal/mol)
C_2NCCO_2C	-88.53[a] ± 0.19	CCOH	-56.23[b] ± 0.12
CCOC(O)C	-106.46[c] ± 0.20	C_jCOH	-5.83[d] ± 0.12
$CC_jOC(O)C$	-60.86[f] ± 0.20	$CCOC(O)C_j$	-59.57[h] ± 0.20
CH_3NH_2	-5.50[i]	CH_3N_jH	43.26[j]
$CH_{2j}NH_2$	36.26[j]	CH_4	-17.8 ± 0.1[k]
CH_3CH_3	-20.0 ± 0.1[k]	CCN	-11.3 ± 0.17[l]
CCNC	-11.29[m] ± 0.44	C_2NC	-5.67 ± 0.18[n]
CCCN	-16.7 ± 0.2[p]		

[a] Reference 17 [b] Reference 18 [c] Reference 19

[d] CCOH = CjCOH + H
ΔH_{Rxn} = Bond Energy = 102.5[e] kcal/mol
CjCOH = -56.23[b] ± 0.12 –52.1 + 102.5 = -5.83 ± 0.12 kcal/mol

[e] Reference 20

[f] CCOC(O)C = CCjOC(O)C + H
ΔH_{Rxn} = Bond Energy = 97.7 kcal/mol
CCjOC(O)C = -106.46[c] ± 0.20 –52.1 + 97.7 = -60.86 ± 0.20 kcal/mol

[h] CCOC(O)C = CCOC(O)Cj + H
ΔH_{Rxn} = Bond Energy = 98.99[g] kcal/mol
CCOC(O)Cj = -106.46[c] ± 0.20 –52.1 + 98.99 = -59.57 ± 0.20 kcal/mol

[i] Reference 21 [j] THERM[22] [k] Reference 23 [l] Reference 24
[m] calculated at the B3LYP/6-31 G(d,p) level using the isodesmic reaction: CCNC + C = CCN + CC
[n] Reference 25 [p] Reference 26

Enthalpies of formation ($\Delta H^0_{f(298)}$) are estimated using total energies and calculated ΔH^0_{rxn} 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 $\Delta H^0_{f(298)}$ 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]
$CCNCO_2CC$	0.165264	-402.234151	-402.223615	6.61	101.69
C_2NC	0.120602	-174.365569	-174.359209	3.99	74.21
C_2NCCO_2C	0.164269	-402.19429	-402.183661	6.67	101.08
CCNC	0.121186	-174.37237	-174.365818	4.11	74.57
$CCCNCO_2C$	0.165155	-402.228878	-402.218128	6.75	101.63
CCCN	0.121594	-174.378298	-174.371714	4.13	74.82
CH3NH2	0.064205	-95.799481	-95.795143	2.72	39.51
CH3NjH	0.048905	-95.149173	-95.14479	2.75	30.09
CH2jNH2	0.050349	-95.154985	-95.15065	2.72	30.98
$CCNjCO_2CC$	0.151082	-401.572552	-401.562001	6.62	92.97
$CCjNCO_2CC$	0.151135	-401.587572	-401.576823	6.75	93.00
$CjCNCO_2CC$	0.150096	-401.574408	-401.563585	6.79	92.36
CH3CH2OH	0.080164	-154.966045	-154.960823	3.28	49.33
CH2jCH2OH	0.064027	-154.306124	-154.301068	3.17	39.40
$CCNCO_2CjC$	0.150598	-401.579456	-401.568642	6.79	92.67
$CCNCO_2CCj$	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
$CCCNjCO_2C$	0.151021	-401.567409	-401.556692	6.73	92.93
$CCCNCO_2C$	0.165155	-402.228878	-402.218128	6.75	101.63
$CCCjNCO_2C$	0.150971	-401.581789	-401.570808	6.89	92.90

[a]Optimized at the B3LYP/6-31 G(d,p) level of theory, [b]ZPVE : Zero Point Correction in Hartree/Particle, [c]Sum of elec = Sum of electronic and zero-point energies in kcal/mol, [d]Sum of zpe = Sum of electronic and thermal enthalpies, [e]Thermal Corr: Thermal Corrections in Hartree, [f]scaled 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]
$CCNCO_2CC$	-402.3994148	-402.2268209
C_2NC	-174.4861714	-174.3615491
C_2NCCO_2C	-402.3585599	-402.18684872
CCNC	-174.4935563	-174.36816931
$CCCNCO_2C$	-402.3940332	-402.2213322
CCCN	-174.4998925	-174.3740734
CH_3NH_2	-95.863686	-95.7963886
CH_3NjH	-95.1980779	-95.14573866
CH_2jNH_2	-95.2053339	-95.15162667
$CCNjCO_2CC$	-401.7236339	-401.5649319
$CCjNCO_2CC$	-401.7387072	-401.5797552
$CjCNCO_2CC$	-401.7245038	-401.5664967
CH_3CH_2OH	-155.0462094	-154.9623786
CH_2jCH_2OH	-154.3701511	-154.301068
$CCNCO_2CjC$	-401.7300536	-401.5715632
$CCNCO_2CCj$	-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
$CCCNjCO_2C$	-401.7184303	-401.5596221
$CCCNCO_2C$	-402.3940332	-402.2213322
$CCCjNCO_2C$	-401.7327609	-401.5737377

[a] Hf in Hartree [b] B3LYP/6-31 G(d,p). Total Energies are in Hartree at 0 K

The ΔH^0_{rxn} and $\Delta H^0_{f(298)}$ for the urethanes, Ethyl N Ethyl Carbamate ($CCNCO_2CC$), N (n-propyl) Methyl Carbamate ($CCCNCO_2C$) and the corresponding radicals calculated at the B3LYP/6-31 G(d,p) are presented in Table 3.6. The $\Delta H^0_{rxn\,(298)}$ and $\Delta H^0_{f\,(298)}$ for the two urethanes and the radicals are also calculated in MOPAC[1] and are presented in Table 3.7 and Table 3.8 for comparison purposes. One reaction (example), used to calculate $\Delta H^0_{f(298)}$ ($CCNjCO_2CC$) is:

$$CCN_jCO_2CC + CH_3NH_2 \rightarrow CCNCO_2CC + CH_3N_jH$$

$$\Delta H^0_{f\,(298)} = \Delta H^0_{f\,(298)\,(CCNCO2CC)} + \Delta H^0_{f\,(298)\,(CH3NjH)} - (\Delta H^0_{f\,(298)\,(CCNjCO2CC)} + \Delta H^0_{f\,(298)\,(CH3NH2)})$$

Table 3.6 Reaction Enthalpies and Enthalpies of Formation

Isodesmic Reactions	ΔH_{rxn} B3LYP/ 6-31 G(d,p) kcal/mol	$\Delta H^0_{f\,(298)}$ 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
$CC_jNCO_2CC + CH_3NH_2 \rightarrow CCNCO_2CC + CH_{2j}NH_2$	-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
$CCC_jNCO_2C + CH_3NH_2 \rightarrow CCCNCO_2C + CH_{2j}NH_2$	-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 $\Delta H^0_{f(298)}$ values are –115.08 kcal/mol for $CCNCO_2CC$, -113.34 kcal/mol for $CCCNCO_2C$, -59.27 kcal/mol for CCN_jCO_2CC, -71.87 kcal/mol for CC_jNCO_2CC, -64.52 kcal/mol for C_jCNCO_2CC, -64.95 kcal/mol for $CCNCO_2C_jC$, -62.45 kcal/mol for $CCNCO_2CC_j$, -57.64 kcal/mol for $CCCN_jCO_2C$ and –69.80 kcal/mol for CCC_jNCO_2C.

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
CCN_jCO_2CC	-61.84	CC_jNCO_2CC	-73.31
C_jCNCO_2CC	-62.486	$CCNCO_2C_jC$	-66.62
$CCNCO_2CC_j$	-58.52	$CCCN_jCO_2C$	-67.82
CCC_jNCO_2C	-72.38	C_2NCCO_2C	-89.58
CCNC	-12.25	C_2NC	-10.83
CH_3NH_2	-5.18	CH_3N_jH	27.58
$CH_{2j}NH_2$	20.77	CCOH	-56.852
C_jCOH	-20.811	CCOC(O)C	-97.69
$CC_jOC(O)C$	-70.53	CCOC(O)C	-57.84
CCCN	-14.96		

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

Isodesmic Reaction	ΔH_{rxn} kcal/mol	$\Delta H^0_{f(298)}$ kcal/mol
$CCN_jCO_2CC + CH_3NH_2 \rightarrow CCNCO_2CC + CH_3N_jH$	-0.46	-48.66
$CC_jNCO_2CC + CH_3NH_2 \rightarrow CCNCO_2CC + CH_{2j}NH_2$	4.2	-60.32
$C_jCNCO_2CC + CCOH \rightarrow CCNCO_2CC + C_jCOH$	3.47	-50.95
$CCNCO_2C_jC + CCOC(O)C \rightarrow CCNCO_2CC + CC_jOC(O)C$	-1.28	-51.0
$CCNCO_2CC_j + CCOC(O)C \rightarrow CCNCO_2CC + CCOC(O)C_j$	3.31	-54.3
$CCCN_jCO_2C + CH_3NH_2 \rightarrow CCCNCO_2C + CH_3N_jH$	0.73	-57.67
$CCC_jNCO_2C + CH_3NH_2 \rightarrow CCCNCO_2C + CH_{2j}NH_2$	-1.52	-62.74

The $\Delta H^0_{f(298)}$ 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≤T/K≤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
$CCNCO_2CC$	9	92.28	35.41	44.44	52.72	59.83	70.96	79.12	91.68
$CCCNCO_2C$	9	93.44	35.50	44.35	52.57	59.68	70.86	79.05	91.67
$CCNjCO_2CC$	9	95.05	34.58	43.16	51.03	57.76	68.22	75.84	87.43
$CCjNCO_2CC$	9	94.11	35.85	44.25	51.86	58.35	68.48	75.89	87.30
CjCNCO2CC	6	95.76	36.21	44.77	52.41	58.87	68.87	76.17	87.44
$CCNCO_2CjC$	9	94.93	36.00	44.46	52.07	58.55	68.64	76.01	87.37
$CCNCO_2CCj$	6	97.56	36.51	44.99	52.58	59.00	68.97	76.24	87.47
$CCCNjCO_2C$	9	96.13	34.63	43.05	50.87	57.61	68.12	75.78	87.42
$CCCjNCO_2C$	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. [b]Units 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 $\Delta H^0_{f(298)}$ 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.

$$CCNCO_2CC \rightarrow CCN_jCO_2CC + H$$

-114.75 -58.94 52.1(kcal/mol)

ΔH_{Rxn} = Bond Energy= -58.94 + 52.1 + 114.75 = 107.91 kcal/mol = 453.2 kJ/mol

Table 3.10 Bond Energies[a]

	B. E. (kcal/mol)	**B. E. (kJ/mol)**
$CCNCO_2CC \rightarrow CCNjCO_2CC + H$	107.91	453.23
$CCNCO_2CC \rightarrow CCjNCO_2CC + H$	95.31	400.28
$CCNCO_2CC \rightarrow CjCNCO_2CC + H$	102.46	430.33
$CCNCO_2CC \rightarrow CCNCO_2CjC + H$	102.23	429.37
$CCNCO_2CC \rightarrow CCNCO_2CCj + H$	104.73	438.84
$CCCNCO_2C \rightarrow CCCNjCO_2C + H$	107.80	452.76
$CCCNCO_2C \rightarrow CCCjNCO_2C + H$	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_jH-NH-C(O)-O-CH_2-CH_3	363.17	400.3	402.1
C_jH_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_jH-CH_3	415.7	429.4	416.9
CH_3-CH_2-NH-C(O)-O-CH_2-C_jH_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_jH-NH-C(O)-O-CH_3	408.87	401.7	401.7

[a][27].

CHAPTER 4

CONCLUSION

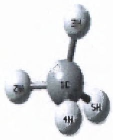
Thermodynamic properties of $CCNCO_2CC$, $CCCNCO_2C$ and the corresponding radicals are calculated at the B3LYP/6-31G(d,p) density functional level and with isodesmic reaction schemes. $\Delta H^0_{f(298)}$ values calculated are –115.08 kcal/mol for $CCNCO_2CC$, -113.34 kcal/mol for $CCCNCO_2C$, -59.27 kcal/mol for CCN_jCO_2CC, -71.87 kcal/mol for CC_jNCO_2CC, -64.52 kcal/mol for C_jCNCO_2CC, -64.95 kcal/mol for $CCNCO_2C_jC$, -62.45 kcal/mol for $CCNCO_2CC_j$, -57.64 kcal/mol for $CCCN_jCO_2C$ and –69.80 kcal/mol for CCC_jNCO_2C. S^0_{298} 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.

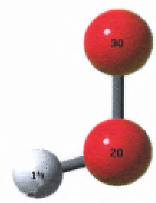
SECTION I

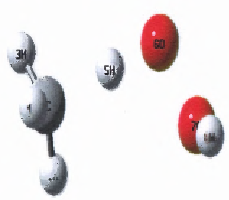
APPENDIX A

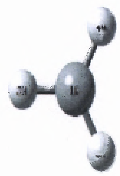
Appendix A consists of eight parts. A.1 lists the optimized geometry parameters of the compounds and the transition states in the hydrogen abstraction reactions considered in this study at the B3LYP/6-311G(d,p) density calculation level. A.2 has the illustrations of the optimized geometries of the transition 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.

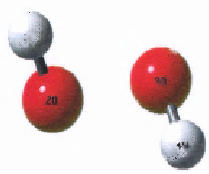
A.1 Geometry Parameters Optimized at the B3LYP/6-311G(d,p) Level

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 [e]		
	A2	A(2,1,4)	109.4692			
	A3	A(3,1,4)	109.4712	158.06031	158.05811	158.05293
	A4	A(2,1,5)	109.4692			
	A5	A(3,1,5)	109.4712			
	A6	A(4,1,5)	109.4717			

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 [e]		
				622.28863	33.70043	31.96912

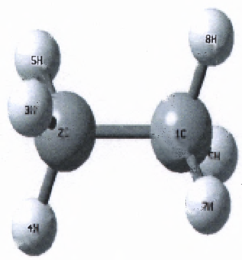
Species and Structure **A.1.3 T C-HOOH**	Name	Definition	Value	Frequencies [d]		
	R[a]1	R(1,2)	1.086	-1435.3193	29.7336	155.2882
	R2	R(2,3)	1.0856	328.4010	447.8372	510.6830
	R3	R(2,4)	1.0855	604.1934	965.9512	982.5885
	R4	R(2,5)	1.441	1176.6383	1382.7102	1418.3779
	R5	R(5,6)	1.1112	1419.8004	1473.9434	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 [e]		
	A2	A(1,2,4)	115.8747			
	A3	A(1,2,5)	99.5571	30.99933	5.42806	4.84144
	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			
	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_3j**	Name Definition Value	Frequencies[d]
	R[a]1 R(2,1) 1.0804 R2 R(3,1) 1.0805 R3 R(4,1) 1.0805 A[b]1 A(2,1,3) 120.0027 A2 A(2,1,4) 120.0026 A3 A(3,1,4) 119.9943 D[c]1 D(2,4,1,3) 180.2362	505.1162 1403.2028 1403.2949 3103.9201 3282.8597 3282.9716 Moments of inertia [e] 286.38337 286.35565 143.18508

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

Species and Structure

A.1.6 C_2H_6



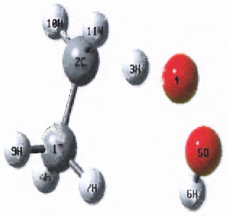
Name	Definition	Value
R[a]1	R(2,1)	1.5304
R2	R(3,2)	1.0936
R3	R(4,2)	1.0936
R4	R(5,2)	1.0936
R5	R(6,1)	1.0936
R6	R(7,1)	1.0936
R7	R(8,1)	1.0936
A[b]1	A(1,2,3)	111.3661
A2	A(1,2,4)	111.3786
A3	A(3,2,4)	107.5053
A4	A(1,2,5)	111.374
A5	A(3,2,5)	107.5031
A6	A(4,2,5)	107.5049
A7	A(2,1,6)	111.3663
A8	A(2,1,7)	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[c]1	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

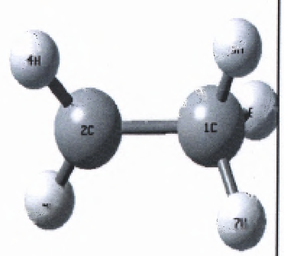
Frequencies[d]

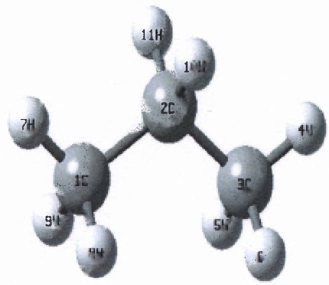
305.8654	826.8498	827.5076
997.5961	1218.6842	1219.5010
1409.7483	1425.3385	1504.6720
1504.9147	1507.1829	1507.8182
3025.0210	3025.6840	3070.9292
3071.1152	3096.2724	3096.4223

Moments of inertia[e]

80.58815	19.91540	19.91524

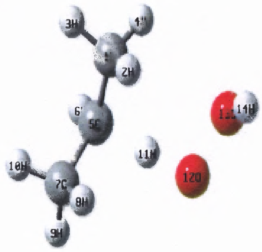
Species and Structure **A.1.7 T CC-HOOH**	Name	Definition	Value	Frequencies [d]		
	R[a]1	R(1,2)	1.5022	-1602.7444	52.3031	115.3390
	R2	R(1,7)	1.0936	162.7953	262.3167	390.6833
	R3	R(1,8)	1.0932	500.6567	563.9687	828.6246
	R4	R(1,9)	1.0991	872.1334	984.3343	1028.9604
	R5	R(2,3)	1.3955	1069.8875	1196.2906	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]		
	A2	A(2,1,8)	111.6907			
	A3	A(2,1,9)	111.012	12.65842	3.52166	2.95398
	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_2H_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]		
	A2	A(1,2,4)	121.6996			
	A3	A(3,2,4)	117.7331	103.92564	22.71349	21.04061
	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	Name	Definition	Value	Frequencies[d]		
A.1.9 CCC						
	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]		
	A2	A(2,1,8)	111.1159			
	A3	A(2,1,9)	111.1136	29.53151	8.36726	7.41678
	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_2C-HOOH



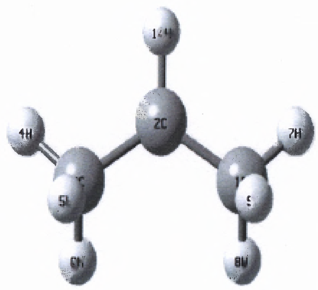
Name	Definition	Value
R[a]1	R(1,2)	1.0946
R2	R(1,3)	1.0993
R3	R(1,4)	1.0929
R4	R(1,5)	1.5075
R5	R(5,6)	1.0924
R6	R(5,7)	1.5081
R7	R(5,11)	1.3638
R8	R(7,8)	1.0941
R9	R(7,9)	1.0926
R10	R(7,10)	1.0996
R11	R(11,12)	1.1714
R12	R(12,13)	1.4141
R13	R(13,14)	0.9679
A[b]1	A(2,1,3)	107.184
A2	A(2,1,4)	108.4816
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

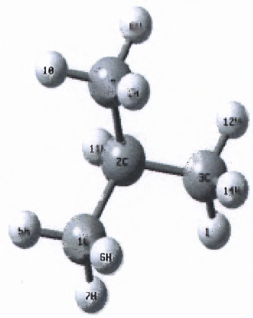
Frequencies [d]

-1656.7388	38.2478	100.9694
151.0334	188.8173	210.1366
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

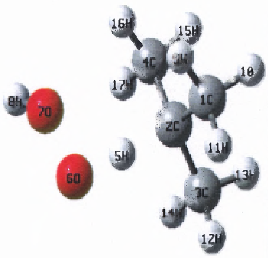
Moments of inertia [e]

6.89582	2.44068	1.93365

Species and Structure **A.1.11 CC$_i$C**	Name	Definition	Value	Frequencies [d]		
	R[a]1	R(1,2)	1.4904	103.4692	115.2256	352.6971
	R2	R(1,7)	1.0929	394.9236	883.1311	939.1887
	R3	R(1,8)	1.0975	944.7625	1028.0522	1146.2080
	R4	R(1,9)	1.1036	1177.6171	1367.2612	1408.1946
	R5	R(2,3)	1.4904	1412.6782	1469.5280	1477.9005
	R6	R(2,10)	1.0847	1480.2079	1491.7114	2931.7777
	R7	R(3,4)	1.0929	2936.3712	3010.9290	3012.1614
	R8	R(3,5)	1.1036	3081.8900	3082.7985	3163.0778
	R9	R(3,6)	1.0975			
	A[b]1	A(2,1,7)	112.0356	Moments of inertia [e]		
	A2	A(2,1,8)	111.5715			
	A3	A(2,1,9)	112.0209	37.47493	8.31449	7.43320
	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			

Species and Structure **A.1.12 C_3C**	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]		
	A2	A(2,1,6)	110.8263			
	A3	A(2,1,7)	111.3344	7.75218	7.75089	4.48612
	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 C_3C-HOOH		



Name	Definition	Value
R[a]1	R(1,2)	1.5144
R2	R(1,9)	1.0928
R3	R(1,10)	1.0998
R4	R(1,11)	1.0927
R5	R(2,3)	1.5145
R6	R(2,4)	1.5143
R7	R(2,5)	1.3369
R8	R(3,12)	1.0931
R9	R(3,13)	1.0999
R10	R(3,14)	1.0933
R11	R(4,15)	1.0996
R12	R(4,16)	1.0935
R13	R(4,17)	1.0935
R14	R(5,6)	1.1971
R15	R(6,7)	1.4127
R16	R(7,8)	0.968
A[b]1	A(2,1,9)	111.2994
A2	A(2,1,10)	110.4524
A3	A(2,1,11)	111.4522
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
A8	A(1,2,4)	114.8109
A9	A(1,2,5)	102.2391
A10	A(3,2,4)	115.2622
A11	A(3,2,5)	103.9597
A12	A(4,2,5)	102.6884
A13	A(2,3,12)	111.5453
A14	A(2,3,13)	110.4125
A15	A(2,3,14)	111.624
A16	A(12,3,13)	107.3657
A17	A(12,3,14)	108.2943
A18	A(13,3,14)	107.4097
A19	A(2,4,15)	110.6886
A20	A(2,4,16)	111.1424
A21	A(2,4,17)	111.56
A22	A(15,4,16)	107.2815
A23	A(15,4,17)	107.4389
A24	A(16,4,17)	108.5541
A25	A(5,6,7)	104.5824
A26	A(6,7,8)	102.3879
A27	L(2,5,6,3,-1)	182.9553
A28	L(2,5,6,3,-2)	181.4181

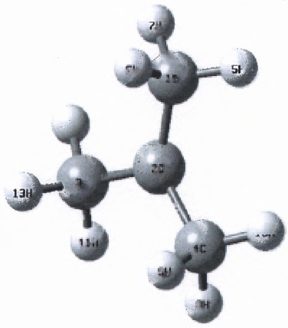
Frequencies [d]

-1638.9943	33.9487	91.8919
122.8722	181.3166	206.1979
212.1653	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

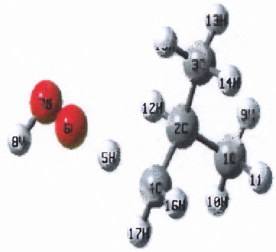
Moments of inertia [e]

4.11953	1.86835	1.82324

Name	Definition	Value
D[c]1	D(9,1,2,3)	-170.2112
D2	D(9,1,2,4)	52.2
D3	D(9,1,2,5)	-58.1586
D4	D(10,1,2,3)	70.259
D5	D(10,1,2,4)	-67.3298
D6	D(10,1,2,5)	-177.6883
D7	D(11,1,2,3)	-49.3507
D8	D(11,1,2,4)	173.0605
D9	D(11,1,2,5)	62.702
D10	D(1,2,3,12)	50.8233
D11	D(1,2,3,13)	-68.4728
D12	D(1,2,3,14)	172.1248
D13	D(4,2,3,12)	-171.7811
D14	D(4,2,3,13)	68.9228
D15	D(4,2,3,14)	-50.4796
D16	D(5,2,3,12)	-60.2153
D17	D(5,2,3,13)	-179.5114
D18	D(5,2,3,14)	61.0862
D19	D(1,2,4,15)	65.3546
D20	D(1,2,4,16)	-53.7564
D21	D(1,2,4,17)	-175.0639
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_3Cj**	Name	Definition	Value	Frequencies [d]		
	R[a]1	R(1,2)	1.4952	129.4656	130.2361	134.7476
	R2	R(1,5)	1.0949	261.2783	379.4233	380.3539
	R3	R(1,6)	1.1051	757.2204	935.4122	936.1775
	R4	R(1,7)	1.0946	970.4860	1006.0558	1007.2579
	R5	R(2,3)	1.4952	1093.1767	1292.5659	1293.2965
	R6	R(2,4)	1.4952	1396.6085	1397.2466	1424.2066
	R7	R(3,11)	1.0946	1469.1088	1470.9600	1471.7928
	R8	R(3,12)	1.0949	1489.8591	1492.7254	1493.5284
	R9	R(3,13)	1.1052	2915.4181	2915.6906	2924.5464
	R10	R(4,8)	1.0947	3028.5825	3028.8524	3031.7821
	R11	R(4,9)	1.1051	3071.2994	3076.1501	3076.2752
	R12	R(4,10)	1.0948			
	A[b]1	A(2,1,5)	111.7545	Moments of inertia [e]		
	A2	A(2,1,6)	111.9057			
	A3	A(2,1,7)	111.7756	7.98741	7.97909	4.32905
	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[c]1	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			

Molecule	Name Definition Value	Frequencies [d]
A.1.15 C_2CC-HOOH		



Name	Definition	Value
R[a]1	R(1,2)	1.545
R2	R(1,9)	1.0943
R3	R(1,10)	1.0933
R4	R(1,11)	1.0944
R5	R(2,3)	1.5344
R6	R(2,4)	1.5093
R7	R(2,12)	1.0973
R8	R(3,13)	1.0933
R9	R(3,14)	1.0955
R10	R(3,15)	1.0919
R11	R(4,5)	1.3946
R12	R(4,16)	1.0914
R13	R(4,17)	1.0906
R14	R(5,6)	1.1462
R15	R(6,7)	1.4162
R16	R(7,8)	0.968
A[b]1	A(2,1,9)	110.3114
A2	A(2,1,10)	111.5246
A3	A(2,1,11)	110.861
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
A8	A(1,2,4)	110.2959
A9	A(1,2,12)	107.5309
A10	A(3,2,4)	111.5623
A11	A(3,2,12)	108.2529
A12	A(4,2,12)	107.6323
A13	A(2,3,13)	111.0298
A14	A(2,3,14)	110.7727
A15	A(2,3,15)	110.746
A16	A(13,3,14)	107.7784
A17	A(13,3,15)	108.2795
A18	A(14,3,15)	108.1172
A19	A(2,4,5)	104.6476
A20	A(2,4,16)	116.4089
A21	A(2,4,17)	116.3702
A22	A(5,4,16)	101.7441
A23	A(5,4,17)	101.5968
A24	A(16,4,17)	113.1609
A25	A(5,6,7)	104.6896
A26	A(6,7,8)	102.2382
A27	L(4,5,6,2,-1)	176.0674
A28	L(4,5,6,2,-2)	178.0098

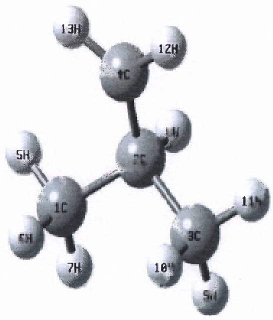
Frequencies [d]

-1603.6678	35.3058	51.9104
101.9008	193.8203	225.5729
259.2589	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

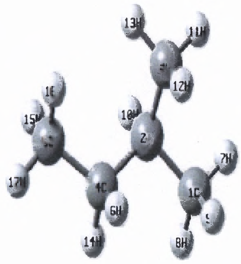
Moments of inertia [e]

5.43695	1.50390	1.41560

Name	Definition	Value
D[c]1	D(9,1,2,3)	-57.7041
D2	D(9,1,2,4)	177.8487
D3	D(9,1,2,12)	60.7506
D4	D(10,1,2,3)	-177.7258
D5	D(10,1,2,4)	57.827
D6	D(10,1,2,12)	-59.271
D7	D(11,1,2,3)	61.8356
D8	D(11,1,2,4)	-62.6117
D9	D(11,1,2,12)	-179.7097
D10	D(1,2,3,13)	59.1042
D11	D(1,2,3,14)	-60.6118
D12	D(1,2,3,15)	179.4331
D13	D(4,2,3,13)	-177.1643
D14	D(4,2,3,14)	63.1197
D15	D(4,2,3,15)	-56.8354
D16	D(12,2,3,13)	-58.9165
D17	D(12,2,3,14)	-178.6325
D18	D(12,2,3,15)	61.4124
D19	D(1,2,4,5)	-171.3098
D20	D(1,2,4,16)	77.3019
D21	D(1,2,4,17)	-60.1184
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_3jC**	Name	Definition	Value	Frequencies [d]		
	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 [e]		
	A2	A(2,1,6)	110.6713			
	A3	A(2,1,7)	111.0346	8.40999	7.88371	4.60287
	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 **A.1.17 C_2CCC**	Name Definition Value	Frequencies [d]



Name	Definition	Value
R[a]1	R(2,1)	1.535
R2	R(3,2)	1.5353
R3	R(4,2)	1.5407
R4	R(5,4)	1.5321
R5	R(6,4)	1.098
R6	R(7,1)	1.094
R7	R(8,1)	1.094
R8	R(9,1)	1.0957
R9	R(10,2)	1.0991
R10	R(11,3)	1.0939
R11	R(12,3)	1.0959
R12	R(13,3)	1.0927
R13	R(14,4)	1.0964
R14	R(15,5)	1.0949
R15	R(16,5)	1.093
R16	R(17,5)	1.0935
A[b]1	A(1,2,3)	110.5167
A2	A(1,2,4)	110.5719
A3	A(3,2,4)	112.4827
A4	A(2,4,5)	115.0527
A5	A(2,4,6)	108.7553
A6	A(5,4,6)	109.5535
A7	A(2,1,7)	111.3206
A8	A(2,1,8)	111.4038
A9	A(7,1,8)	107.825
A10	A(2,1,9)	110.8353
A11	A(7,1,9)	107.5986
A12	A(8,1,9)	107.6829
A13	A(1,2,10)	107.7717
A14	A(3,2,10)	107.8462
A15	A(4,2,10)	107.4526
A16	A(2,3,11)	110.9205
A17	A(2,3,12)	110.7154
A18	A(11,3,12)	107.5874
A19	A(2,3,13)	112.1897
A20	A(11,3,13)	107.4557
A21	A(12,3,13)	107.7778
A22	A(2,4,14)	108.3488
A23	A(5,4,14)	108.7557
A24	A(6,4,14)	105.9858
A25	A(4,5,15)	111.0919
A26	A(4,5,16)	112.1059
A27	A(15,5,16)	107.6613
A28	A(4,5,17)	110.914
A29	A(15,5,17)	107.5442
A30	A(16,5,17)	107.3121

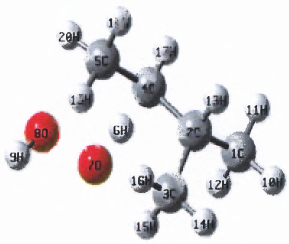
94.4638	212.7540	223.4997
254.4034	263.1714	366.3720
413.5641	456.0860	763.7872
798.9095	912.3936	931.2353
964.9641	987.1926	1024.9266
1043.1989	1167.3576	1192.9927
1202.8157	1297.7670	1328.2502
1370.3899	1382.7363	1402.4836
1412.9017	1421.7824	1483.9120
1490.7065	1497.9763	1501.4641
1506.3724	1509.8519	1514.8126
2982.2128	2999.5624	3012.2314
3017.8999	3021.4656	3030.8150
3070.9776	3077.1098	3080.6109
3082.3458	3086.5007	3094.2830

Moments of inertia [e]

7.26878 3.32594 2.54294

D[c]1	D(3,2,1,7)	-57.0994
D2	D(3,2,1,8)	-177.4924
D3	D(3,2,1,9)	62.6233
D4	D(4,2,1,7)	177.6915
D5	D(4,2,1,8)	57.2985
D6	D(4,2,1,9)	-62.5858
D7	D(10,2,1,7)	60.5176
D8	D(10,2,1,8)	-59.8754
D9	D(10,2,1,9)	180.2403
D10	D(11,3,2,1)	55.5556
D11	D(11,3,2,4)	179.6747
D12	D(11,3,2,10)	-62.0156
D13	D(12,3,2,1)	-63.812
D14	D(12,3,2,4)	60.3071
D15	D(12,3,2,10)	178.6168
D16	D(13,3,2,1)	175.7376
D17	D(13,3,2,4)	-60.1433
D18	D(13,3,2,10)	58.1664
D19	D(5,4,2,1)	-172.0648
D20	D(5,4,2,3)	63.8467
D21	D(5,4,2,10)	-54.6943
D22	D(6,4,2,1)	64.645
D23	D(6,4,2,3)	-59.4435
D24	D(6,4,2,10)	-177.9846
D25	D(14,4,2,1)	-50.1291
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	Name Definition Value	Frequencies [d]
A.1.18 T C_2CC-HOOH-C		



Name	Definition	Value
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
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

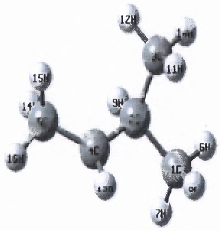
Frequencies [d]

-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

Moments of inertia [e]

2.96239	1.40968	1.21765

Name	Definition	Value
D[c]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_2CCjC**	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 [e]		
	A2	A(2,1,7)	111.1653			
	A3	A(2,1,8)	110.6657	7.45759	3.29782	2.54929
	A4	A(6,1,7)	108.1626			
	A5	A(6,1,8)	107.6898	D[c]1	D(6,1,2,3)	-56.5238
	A6	A(7,1,8)	107.8015	D2	D(6,1,2,4)	178.5867
	A7	A(1,2,3)	110.5491	D3	D(6,1,2,9)	60.0404
	A8	A(1,2,4)	111.6324	D4	D(7,1,2,3)	-177.1082
	A9	A(1,2,9)	108.1312	D5	D(7,1,2,4)	58.0023
	A10	A(3,2,4)	111.6217	D6	D(7,1,2,9)	-60.5441
	A11	A(3,2,9)	106.7813	D7	D(8,1,2,3)	63.1285
	A12	A(4,2,9)	107.9047	D8	D(8,1,2,4)	-61.761
	A13	A(2,3,10)	110.8014	D9	D(8,1,2,9)	179.6927
	A14	A(2,3,11)	110.6407	D10	D(1,2,3,10)	57.9752
	A15	A(2,3,12)	111.387	D11	D(1,2,3,11)	-61.8216
	A16	A(10,3,11)	108.0309	D12	D(1,2,3,12)	178.1129
	A17	A(10,3,12)	107.9103	D13	D(4,2,3,10)	-177.1292
	A18	A(11,3,12)	107.9388	D14	D(4,2,3,11)	63.074
	A19	A(2,4,5)	122.1924	D15	D(4,2,3,12)	-56.9916
	A20	A(2,4,13)	117.8101	D16	D(9,2,3,10)	-59.4227
	A21	A(5,4,13)	118.4989	D17	D(9,2,3,11)	-179.2195
	A22	A(4,5,14)	111.5493	D18	D(9,2,3,12)	60.7149
	A23	A(4,5,15)	112.4273	D19	D(1,2,4,5)	-158.3365
	A24	A(4,5,16)	111.767	D20	D(1,2,4,13)	35.8475
	A25	A(14,5,15)	106.2347	D21	D(3,2,4,5)	77.3737
	A26	A(14,5,16)	108.0591	D22	D(3,2,4,13)	-88.4422
	A27	A(15,5,16)	106.4729	D23	D(9,2,4,5)	-39.6551
				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

[a]Bond Length in A°. [b]Bond angle in degree. [c]Dihedral angle in degree. [d]Frequencies in cm^{-1}. [e]Moments of inertia in amu.$Bohr^2$.

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

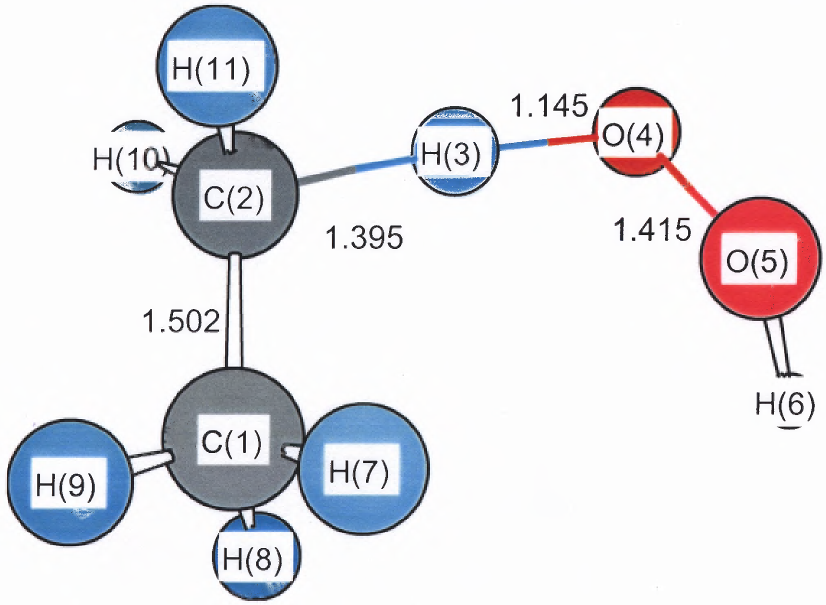


Figure A.1 Geometry of the Transition State T CC-HOOH (distances in Angstroms)

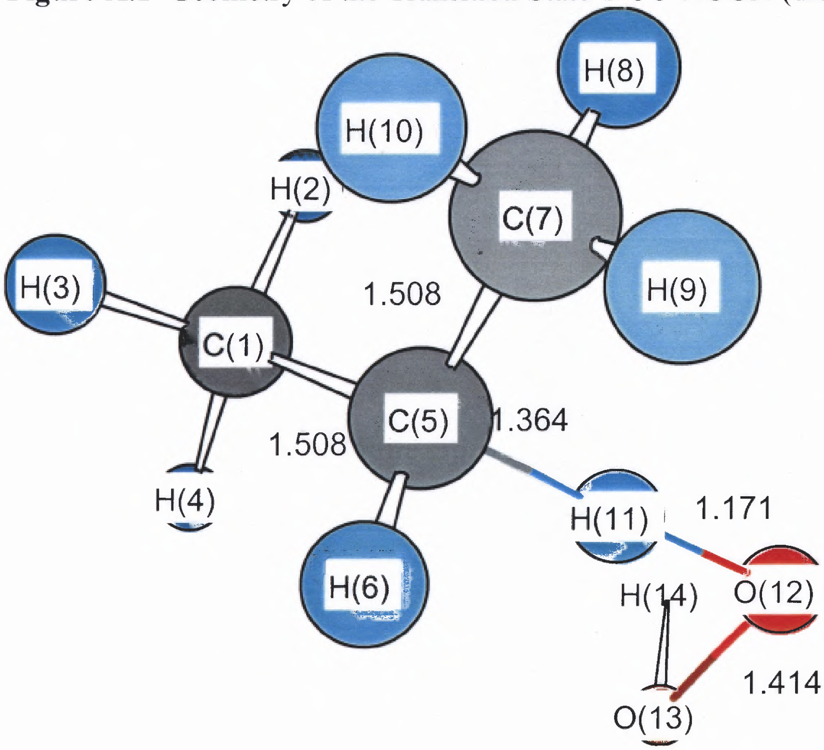


Figure A.2 Geometry of the Transition State T C_2C-HOOH (distances in Angstroms)

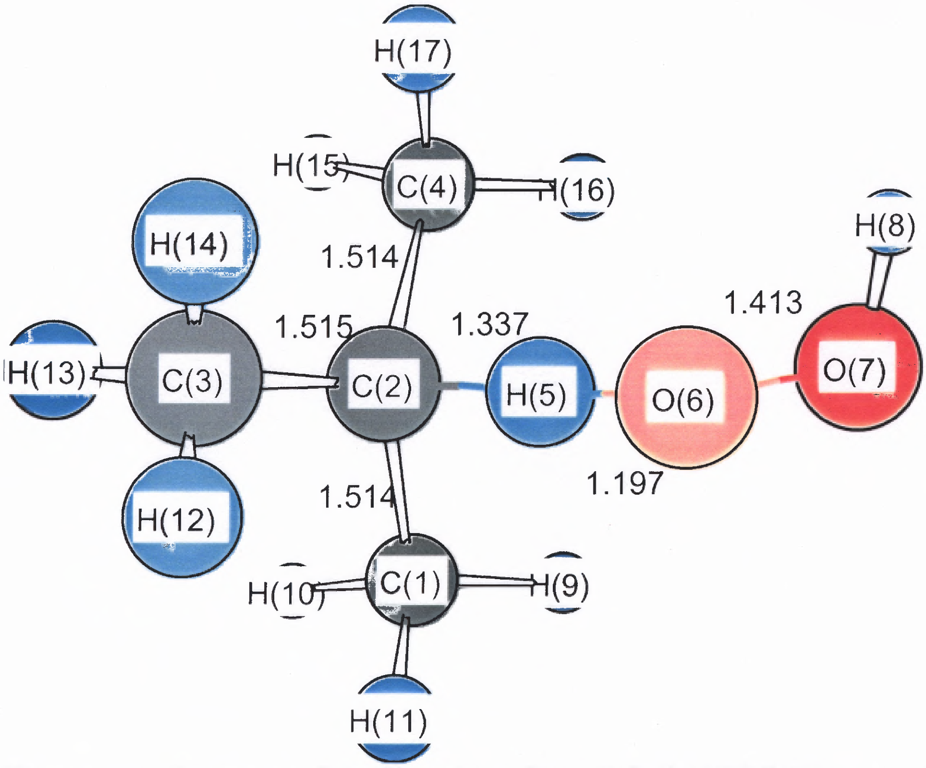


Figure A.3 Geometry of the Transition State T C_3C-HOOH (distances in Angstroms)

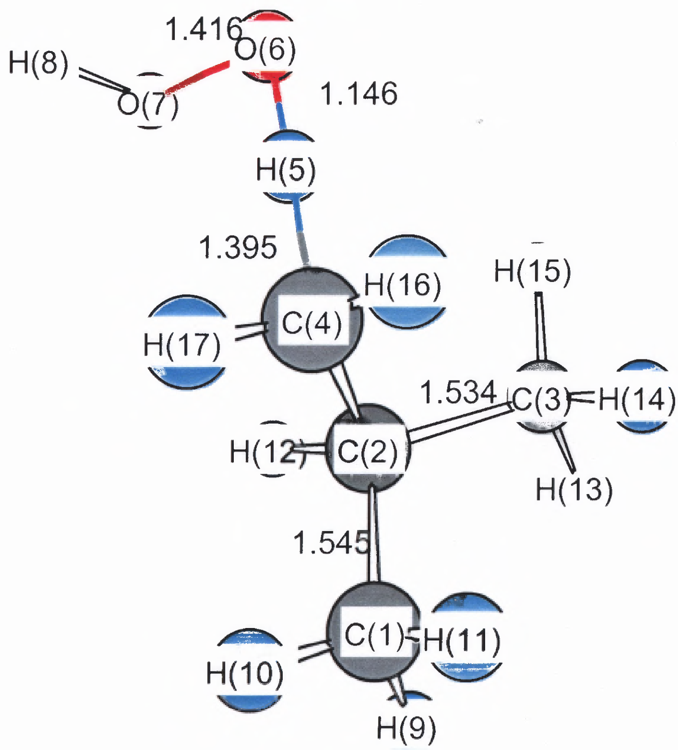


Figure A.4 Geometry of the Transition State C_2CC-HOOH (distances in Angstroms)

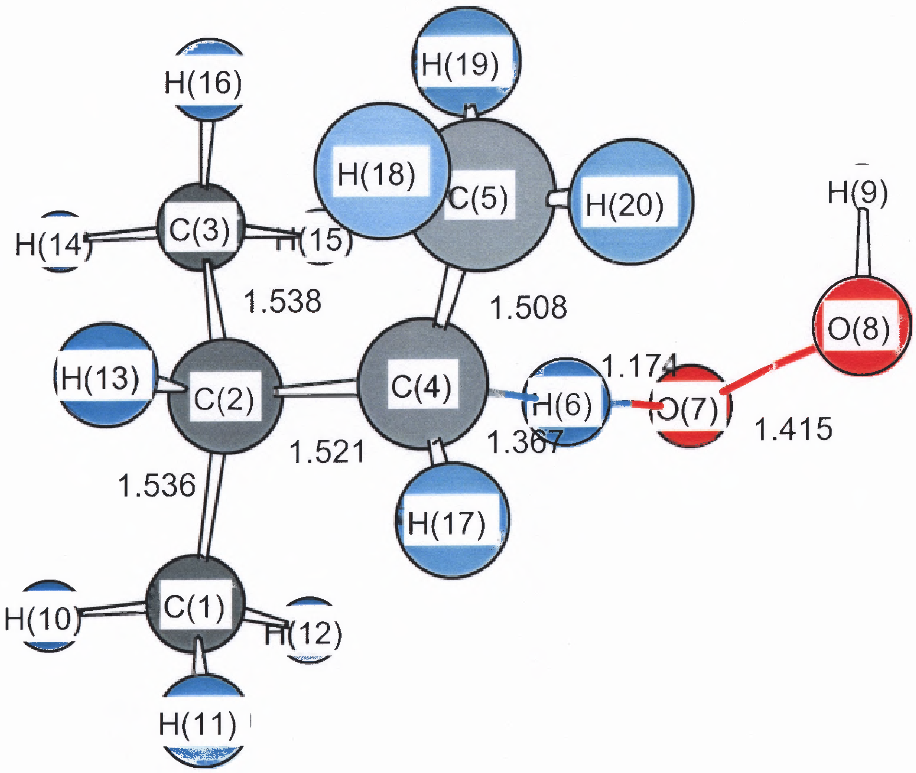


Figure A.5 Geometry of the Transition State C_2CC-HOOHC(distances in Angstroms)

A.3 THERMKIN Calculations (G3MP2 Level)

Three parameters fit model equation: k(T) = A' x T^n x exp(-Ea/RT)

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

	C_2H_6	+	HO_2 →	T CCHOOH
$\Delta H^o_{f\ 298}$ {kcal/mol}	-20.2		3.2	7.20
S^o_{298} {cal/mol K}	54.81		54.380	83.78

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)

	C_2H_5 +	HOOH →	TCCHOOH
Hf {kcal/mol}	28.500	-32.530	7.200
S {cal/mol K}	59.510	55.660	83.780

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)

	CCC +	HO_2 →	T C_2CHOOH
$\Delta H^{o}_{f\ 298}$ {kcal/mol}	-25.33	3.200	1.23
S^{o}_{298} {cal/mol K}	64.50	54.380	91.80

Aprime = 7.1402E+03 n = 2.85325 Ea = 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)

	CC_jC	+ HOOH →	T C_2CHOOH
$\Delta H^{o}_{f\ 298}$ {kcal/mol}	21.020	-32.530	1.230
S^{o}_{298} {cal/mol K}	70.310	55.660	91.800

Aprime = 6.1481E+01 n = 3.00686 Ea = 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)

	C_3C	+	HO_2	→	T C_3CHOOH
$\Delta H^o_{f\ 298}$ {kcal/mol}	-32.500		3.200		-7.970
S^o_{298} {cal/mol K}	70.430		54.380		98.01

Aprime = 3.1822E+03 n = 3.00697 Ea = 2.0822E+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	2.133E+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)

	C_3C_j	+	HOOH	→	T C_3CHOOH
$\Delta H^o_{f\ 298}$ {kcal/mol}	11.700		-32.530		-7.970
S^o_{298} {cal/mol K}	75.670		55.660		98.010

Aprime = 4.4356E+00 n = 3.45615 Ea = 1.1904E+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	1.286E+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)

	C_3C	+ HO_2 →	T $C_2CCHOOH$
$\Delta H^o_{f\ 298}$ {kcal/mol}	-32.500	3.20	-2.82
S^o_{298} {cal/mol K}	70.430	54.380	100.68

Aprime = 6.8657E+03 n = 3.08366 Ea = 2.5888E+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	2.648E+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) $C_{3j}C + HOOH \rightarrow T - C_2CCHOOH$ (reverse reaction)

	$C_{3j}C$	+ HOOH →	T $C_2CCHOOH$
$\Delta H^o_{f\ 298}$ {kcal/mol}	16.500	-32.530	-2.820
S^o_{298} {cal/mol K}	77.40	55.660	100.680

Aprime = 4.4070E+02 n = 2.84324 Ea = 1.2626E+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	1.321E+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) $C_2CCC + HO_2 \rightarrow T - C_2CCHOOHC$ (forward reaction)

	C_2CCC +	HO_2 →	T $C_2CCHOOHC$
$\Delta H^o{}_{f\ 298}$ {kcal/mol}	-37.430	3.20	-9.07
$S^o{}_{298}$ {cal/mol K}	82.03	54.38	107.66

Aprime = 1.7184E+03 n = 2.94685 Ea = 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) $C_2CC_jC + HOOH \rightarrow T - C_2CCHOOHC$ (reverse reaction)

	C_2CC_jC +	HOOH →	T $C_2CCHOOHC$
$\Delta H^o{}_{f\ 298}$ {Kcal/mol}	8.920	-32.530	-9.070
$S^o{}_{298}$ {cal/mol K}	86.470	55.660	107.660

Aprime = 2.9011E+01 n = 3.10271 Ea = 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)

	CH_4	+	HO_2 →	T CHOOH
$\Delta H^o_{f\ 298}$ {kcal/mol}	-17.9		3.2	6.66
S^o_{298}{cal/mol K}	44.49		54.380	73.17

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)

	CH_3	+	HOOH →	T CHOOH
$\Delta H^o_{f\ 298}$ {kcal/mol}	34.820		-32.530	6.660
S^o_{298}{cal/mol K}	46.380		55.660	73.170

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)

	C_2H_6	+	HO_2 →	T CCHOOH
$\Delta H^o{}_{f\ 298}$ {kcal/mol}	-20.2		3.2	0.01
$S^o{}_{298}$ {cal/mol K}	54.81		54.380	83.78

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	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)

	C_2H_5 +	HOOH →	TCCHOOH
Hf {kcal/mol}	28.500	-32.530	0.01
S {cal/mol K}	59.510	55.660	83.780

Aprime = 2.8783E+02 n = 2.95375 Ea = 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)

	CCC +	HO_2 →	T C_2CHOOH
$\Delta H^o_{f\ 298}$ {kcal/mol}	-25.33	3.200	-7.62
S^o_{298} {cal/mol K}	64.50	54.380	91.80

Aprime = 7.1402E+03 n = 2.85325 Ea = 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)

	CC_jC +	HOOH →	T C_2CHOOH
$\Delta H^o_{f\ 298}$ {kcal/mol}	21.020	-32.530	-7.62
S^o_{298} {cal/mol K}	70.310	55.660	91.800

Aprime = 6.1481E+01 n = 3.00686 Ea = 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)

	C_3C	+	HO_2	→	T C_3CHOOH
$\Delta H^o{}_{f\ 298}$ {kcal/mol}	-32.500		3.200		-18.65
$S^o{}_{298}$ {cal/mol K}	70.430		54.380		98.01

Aprime = 3.1822E+03 n = 3.00697 Ea = 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)

	C_3C_j	+ HOOH	→ T C_3CHOOH
$\Delta H^o{}_{f\ 298}$ {kcal/mol}	11.700	-32.530	-18.65
$S^o{}_{298}$ {cal/mol K}	75.670	55.660	98.010

Aprime = 4.4356E+00 n = 3.45615 Ea = 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)

	C_3C	+ HO_2 →	T $C_2CCHOOH$
$\Delta H^o_{f\ 298}$ {kcal/mol}	-32.500	3.20	-13.2
S^o_{298} {cal/mol K}	70.430	54.380	100.68

Aprime = 6.8657E+03 n = 3.08366 Ea = 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) $C_{3j}C + HOOH \rightarrow T - C_2CCHOOH$ (reverse reaction)

	$C_{3j}C$	+ HOOH →	T $C_2CCHOOH$
$\Delta H^o_{f\ 298}$ {kcal/mol}	16.500	-32.530	-13.2
S^o_{298} {cal/mol K}	77.40	55.660	100.68

Aprime = 4.4070E+02 n = 2.84324 Ea = 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 Temparatures

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 HO_2 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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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-C_2C-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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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-C_3C-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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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-C_2CC-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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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 C_2CC-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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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/6-31g*
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.8.2 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)  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.
```

```
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 TC_2CHOOH

```
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*COS(nx)+C*SIN(nx)   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.
```

```
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*COS(nx)+C*SIN(nx)  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*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.8.4 TC_3CHOOH

```
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)  b3lyp/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

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*COS(nx)+C*SIN(nx)  b3lyp/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*COS(nx)+C*SIN(nx)  b3lyp/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.
```

```
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*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.8.5 $TC_2CCHOOH$

```
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*COS(nx)+C*SIN(nx)  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.
```

```
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)  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-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*COS(nx)+C*SIN(nx)  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*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.8.6 $TC_2CCHOOHC$

```
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/6-31g*
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-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*COS(nx)+C*SIN(nx)  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/6-31g*
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.
```

```
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*COS(nx)+C*SIN(nx)  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.
```

```
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*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.
```

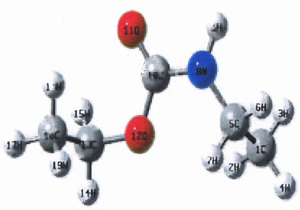
SECTION II

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^0_{298}) 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_2CC

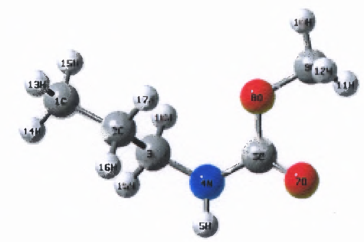


R1	R(1,2)	1.0935
R2	R(1,3)	1.095
R3	R(1,4)	1.0953
R4	R(1,5)	1.5315
R5	R(5,6)	1.0953
R6	R(5,7)	1.0921
R7	R(5,8)	1.4593
R8	R(8,9)	1.0091
R9	R(8,10)	1.3655
R10	R(10,11)	1.2195
R11	R(10,12)	1.362
R12	R(12,13)	1.4445
R13	R(13,14)	1.093
R14	R(13,15)	1.0924
R15	R(13,16)	1.5207
R16	R(16,17)	1.0953
R17	R(16,18)	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 $CCCNCO_2C$

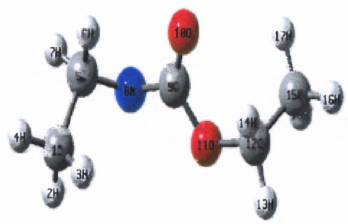


[redacted]

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
A1	A(2,1,13)	111.2056
A2	A(2,1,14)	111.4212
A3	A(2,1,15)	111.2644
A4	A(13,1,14)	107.579
A5	A(13,1,15)	107.6135
A6	A(14,1,15)	107.5634
A7	A(1,2,3)	112.3637
A8	A(1,2,16)	109.961
A9	A(1,2,17)	110.1336
A10	A(3,2,16)	109.1299
A11	A(3,2,17)	108.4121
A12	A(16,2,17)	106.6635
A13	A(2,3,4)	114.2047
A14	A(2,3,18)	109.9604
A15	A(2,3,19)	110.0153
A16	A(4,3,18)	107.9834
A17	A(4,3,19)	107.423
A18	A(18,3,19)	106.9702
A19	A(3,4,5)	118.9754
A20	A(3,4,6)	126.1238
A21	A(5,4,6)	112.9552
A22	A(4,6,7)	124.6373
A23	A(4,6,8)	111.3328
A24	A(7,6,8)	124.0214
A25	A(6,8,9)	114.3447
A26	A(8,9,10)	105.5554
A27	A(8,9,11)	110.8598
A28	A(8,9,12)	110.8732
A29	A(10,9,11)	110.38
A30	A(10,9,12)	110.4775
A31	A(11,9,12)	108.6844

D1	D(13,1,2,3)	-179.8996
D2	D(13,1,2,16)	58.3349
D3	D(13,1,2,17)	-58.9288
D4	D(14,1,2,3)	60.0865
D5	D(14,1,2,16)	-61.6791
D6	D(14,1,2,17)	-178.9428
D7	D(15,1,2,3)	-59.9475
D8	D(15,1,2,16)	178.287
D9	D(15,1,2,17)	61.0233
D10	D(1,2,3,4)	-179.3607
D11	D(1,2,3,18)	59.0792
D12	D(1,2,3,19)	-58.488
D13	D(16,2,3,4)	-57.1231
D14	D(16,2,3,18)	-178.6831
D15	D(16,2,3,19)	63.7497
D16	D(17,2,3,4)	58.6847
D17	D(17,2,3,18)	-62.8753
D18	D(17,2,3,19)	179.5575
D19	D(2,3,4,5)	81.7839
D20	D(2,3,4,6)	-81.1716
D21	D(18,3,4,5)	-155.5725
D22	D(18,3,4,6)	41.4719
D23	D(19,3,4,5)	-40.5176
D24	D(19,3,4,6)	156.5269
D25	D(3,4,6,7)	171.7322
D26	D(3,4,6,8)	-9.2927
D27	D(5,4,6,7)	7.9015
D28	D(5,4,6,8)	-173.1234
D29	D(4,6,8,9)	-177.5995
D30	D(7,6,8,9)	1.3831
D31	D(6,8,9,10)	-179.0865
D32	D(6,8,9,11)	61.3812
D33	D(6,8,9,12)	-59.43028

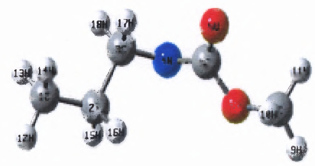
B.1.3 CCN_jCO_2CC



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

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

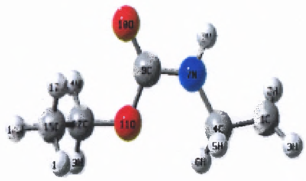
B.1.4 $CCCN_jCO_2C$



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

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

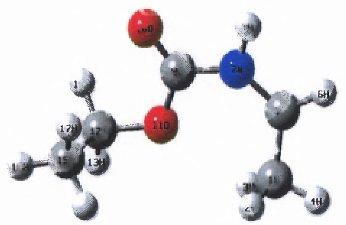
B.1.5 C_jCNCO_2CC



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

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

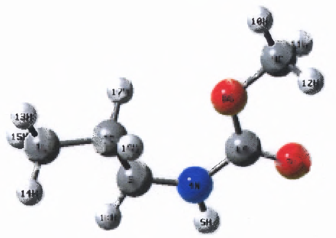
B.1.6 CC_jNCO_2CC



D1	D(2,1,5,6)	102.206
D2	D(2,1,5,7)	-56.1751
D3	D(3,1,5,6)	-137.3936
D4	D(3,1,5,7)	64.2252
D5	D(4,1,5,6)	-17.1862
D6	D(4,1,5,7)	-175.5673
D7	D(1,5,7,8)	164.8558
D8	D(1,5,7,9)	-21.8303
D9	D(6,5,7,8)	5.0254
D10	D(6,5,7,9)	178.3393
D11	D(5,7,9,10)	-177.8
D12	D(5,7,9,11)	2.1584
D13	D(8,7,9,10)	-4.1639
D14	D(8,7,9,11)	175.7945
D15	D(7,9,11,12)	178.325
D16	D(10,9,11,12)	-1.7179
D17	D(9,11,12,13)	155.6778
D18	D(9,11,12,14)	39.0505
D19	D(9,11,12,15)	-83.8838
D20	D(11,12,15,16)	-175.87
D21	D(11,12,15,17)	64.7915
D22	D(11,12,15,18)	-56.1852
D23	D(13,12,15,16)	-59.857
D24	D(13,12,15,17)	-179.1954
D25	D(13,12,15,18)	59.8278
D26	D(14,12,15,16)	62.5331
D27	D(14,12,15,17)	-56.8054
D28	D(14,12,15,18)	-177.7821

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
A1	A(2,1,3)	106.3815
A2	A(2,1,4)	107.742
A3	A(2,1,5)	112.5709
A4	A(3,1,4)	108.2761
A5	A(3,1,5)	112.7998
A6	A(4,1,5)	108.8663
A7	A(1,5,6)	120.1345
A8	A(1,5,7)	124.2463
A9	A(6,5,7)	112.4638
A10	A(5,7,8)	116.7912
A11	A(5,7,9)	132.5961
A12	A(8,7,9)	110.3394
A13	A(7,9,10)	122.3978
A14	A(7,9,11)	112.5593
A15	A(10,9,11)	125.0428
A16	A(9,11,12)	115.4625
A17	A(11,12,13)	104.1647
A18	A(11,12,14)	108.801
A19	A(11,12,15)	111.539
A20	A(13,12,14)	109.4211
A21	A(13,12,15)	111.5347
A22	A(14,12,15)	111.1252
A23	A(12,15,16)	109.8436
A24	A(12,15,17)	110.3642
A25	A(12,15,18)	110.9273
A26	A(16,15,17)	108.2971
A27	A(16,15,18)	108.2913
A28	A(17,15,18)	109.0503

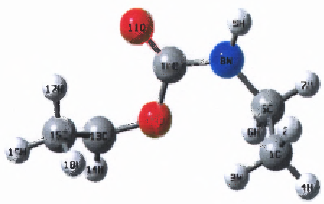
B.1.7 CCC_jNCO_2C



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

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

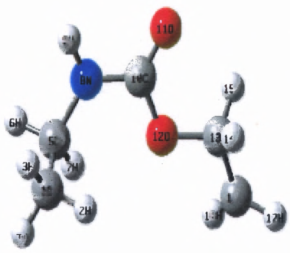
B.1.8 $CCNCO_2C_jC$



D1	D(2,1,5,6)	179.4861
D2	D(2,1,5,7)	61.4441
D3	D(2,1,5,8)	-58.9609
D4	D(3,1,5,6)	-60.2661
D5	D(3,1,5,7)	-178.3081
D6	D(3,1,5,8)	61.287
D7	D(4,1,5,6)	59.4684
D8	D(4,1,5,7)	-58.5736
D9	D(4,1,5,8)	-178.9785
D10	D(1,5,8,9)	84.4219
D11	D(1,5,8,10)	-81.6006
D12	D(6,5,8,9)	-152.7662
D13	D(6,5,8,10)	41.2113
D14	D(7,5,8,9)	-37.7789
D15	D(7,5,8,10)	156.1986
D16	D(5,8,10,11)	173.0877
D17	D(5,8,10,12)	-8.3193
D18	D(9,8,10,11)	6.3406
D19	D(9,8,10,12)	-175.0664
D20	D(8,10,12,13)	178.1018
D21	D(11,10,12,13)	-3.3135
D22	D(10,12,13,14)	158.967
D23	D(10,12,13,15)	-52.2861
D24	D(12,13,15,16)	-176.1856
D25	D(12,13,15,17)	62.959
D26	D(12,13,15,18)	-57.3282
D27	D(14,13,15,16)	-31.1826
D28	D(14,13,15,17)	-152.038
D29	D(14,13,15,18)	87.6748

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
A1	A(2,1,3)	108.2778
A2	A(2,1,4)	108.0937
A3	A(2,1,5)	111.1897
A4	A(3,1,4)	108.2412
A5	A(3,1,5)	110.4691
A6	A(4,1,5)	110.4712
A7	A(1,5,6)	110.275
A8	A(1,5,7)	110.3114
A9	A(1,5,8)	113.8448
A10	A(6,5,7)	107.0546
A11	A(6,5,8)	107.9918
A12	A(7,5,8)	107.0855
A13	A(5,8,9)	119.0176
A14	A(5,8,10)	126.812
A15	A(9,8,10)	112.875
A16	A(8,10,11)	124.6432
A17	A(8,10,12)	110.2124
A18	A(11,10,12)	125.1281
A19	A(10,12,13)	120.1124
A20	A(12,13,14)	109.3218
A21	A(12,13,15)	121.0203
A22	A(14,13,15)	121.3889
A23	A(13,15,16)	109.2084
A24	A(13,15,17)	111.5679
A25	A(13,15,18)	111.7112
A26	A(16,15,17)	109.2363
A27	A(16,15,18)	107.5611
A28	A(17,15,18)	107.4435

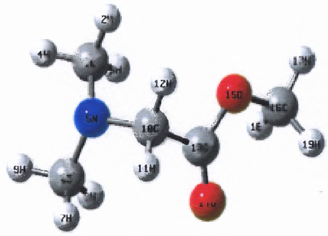
B.1.9 $CCNCO_2CC_j$



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

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

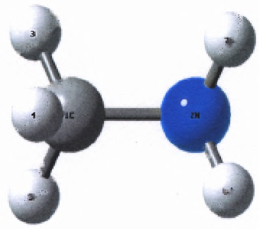
B.1.10 C_2NCCO_2C



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

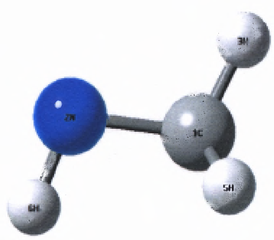
R1	R(1,2)	1.0943
R2	R(1,3)	1.105
R3	R(1,4)	1.0949
R4	R(1,5)	1.4574
R5	R(5,6)	1.4593
R6	R(5,10)	1.4605
R7	R(6,7)	1.0941
R8	R(6,8)	1.1025
R9	R(6,9)	1.0951
R10	R(10,11)	1.0944
R11	R(10,12)	1.0939
R12	R(10,13)	1.5308
R13	R(13,14)	1.2135
R14	R(13,15)	1.3541
R15	R(15,16)	1.4385
R16	R(16,17)	1.0897
R17	R(16,18)	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

B.1.11 CH_3NH_2



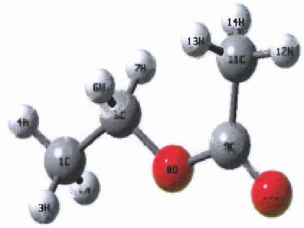
R1	R(1,2)	1.4641
R2	R(1,3)	1.0949
R3	R(1,4)	1.1036
R4	R(1,5)	1.0949
R5	R(2,6)	1.0172
R6	R(2,7)	1.0172
A1	A(2,1,3)	109.2495
A2	A(2,1,4)	115.8558
A3	A(2,1,5)	109.2461
A4	A(3,1,4)	107.5521
A5	A(3,1,5)	107.0295
A6	A(4,1,5)	107.5512
A7	A(1,2,6)	109.7501
A8	A(1,2,7)	109.7467
A9	A(6,2,7)	105.8453
D1	D(3,1,2,6)	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_3N_jH



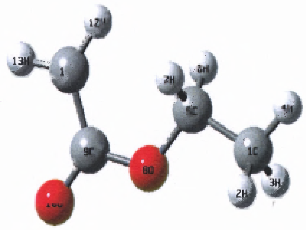
R1	R(1,2)	1.4439
R2	R(1,3)	1.0939
R3	R(1,4)	1.1035
R4	R(1,5)	1.1035
R5	R(2,6)	1.0313
A1	A(2,1,3)	110.5642
A2	A(2,1,4)	111.8021
A3	A(2,1,5)	111.7606
A4	A(3,1,4)	108.3966
A5	A(3,1,5)	108.3805
A6	A(4,1,5)	105.736
A7	A(1,2,6)	105.944
D1	D(3,1,2,6)	179.8797
D2	D(4,1,2,6)	59.0086
D3	D(5,1,2,6)	-59.2977
D6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

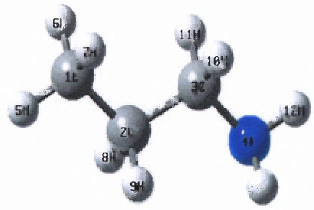
B.1.14 CCOC(O)C_j



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

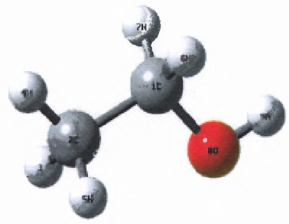
R1	R(1,2)	1.0931
R2	R(1,3)	1.0931
R3	R(1,4)	1.0944
R4	R(1,5)	1.5182
R5	R(5,6)	1.097
R6	R(5,7)	1.097
R7	R(5,8)	1.4379
R8	R(8,9)	1.3619
R9	R(9,10)	1.2068
R10	R(9,11)	1.5166
R11	R(11,12)	1.0889
R12	R(11,13)	1.0946
R13	R(11,14)	1.0946
A1	A(2,1,3)	108.336
A2	A(2,1,4)	108.6009
A3	A(2,1,5)	110.5903
A4	A(3,1,4)	108.6005
A5	A(3,1,5)	110.5933
A6	A(4,1,5)	110.0579
A7	A(1,5,6)	110.6426
A8	A(1,5,7)	110.6403
A9	A(1,5,8)	107.234
A10	A(6,5,7)	108.0576
A11	A(6,5,8)	110.1419
A12	A(7,5,8)	110.136
A13	A(5,8,9)	121.8721
A14	A(8,9,10)	118.6598
A15	A(8,9,11)	117.9832
A16	A(10,9,11)	123.3571
A17	A(9,11,12)	107.9906
A18	A(9,11,13)	111.3641
A19	A(9,11,14)	111.3906
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
			A1	A(1,2,3)	113.0606
			A2	A(2,3,4)	110.7348
			A3	A(2,1,5)	111.3187
			A4	A(2,1,6)	111.2329
D1	D(3,2,1,5)	-179.5088	A5	A(5,1,6)	107.5706
D2	D(3,2,1,6)	60.5385	A6	A(2,1,7)	111.4266
D3	D(3,2,1,7)	-59.4053	A7	A(5,1,7)	107.5861
D4	D(8,2,1,5)	58.8329	A8	A(6,1,7)	107.5062
D5	D(8,2,1,6)	-61.1198	A9	A(1,2,8)	110.5055
D6	D(8,2,1,7)	-181.0636	A10	A(3,2,8)	108.3668
D7	D(9,2,1,5)	-57.8452	A11	A(1,2,9)	109.457
D8	D(9,2,1,6)	-177.7979	A12	A(3,2,9)	108.961
D9	D(9,2,1,7)	62.2582	A13	A(8,2,9)	106.2501
D10	D(4,3,2,1)	-178.1016	A14	A(2,3,10)	108.8937
D11	D(4,3,2,8)	-55.2474	A15	A(4,3,10)	114.0276
D12	D(4,3,2,9)	59.9562	A16	A(2,3,11)	109.0645
D13	D(10,3,2,1)	55.7602	A17	A(4,3,11)	107.6768
D14	D(10,3,2,8)	-181.3856	A18	A(10,3,11)	106.2508
D15	D(10,3,2,9)	-66.182	A19	A(3,4,12)	109.9094
D16	D(11,3,2,1)	-59.7849	A20	A(3,4,13)	109.4359
D17	D(11,3,2,8)	63.0693	A21	A(12,4,13)	105.8871
D18	D(11,3,2,9)	-181.7272			
D19	D(12,4,3,2)	-182.4309			
D20	D(12,4,3,10)	-59.211			
D21	D(12,4,3,11)	58.412			
D22	D(13,4,3,2)	-66.5479			
D23	D(13,4,3,10)	56.672			
D24	D(13,4,3,11)	-185.705			

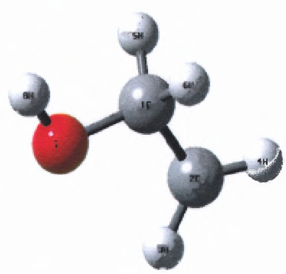
B.1.16 CCOH



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

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

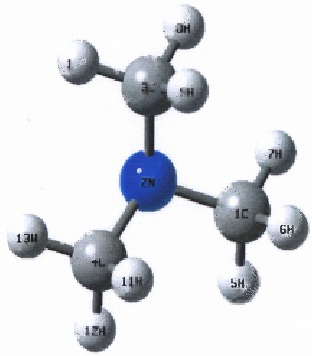
B.1.17 C_jCOH



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

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

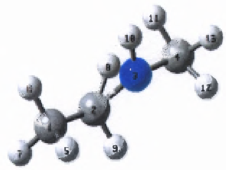
B.1.18 C_2NC



D1	D(3,2,1,5)	-176.6614
D2	D(3,2,1,6)	62.6285
D3	D(3,2,1,7)	-58.0768
D4	D(4,2,1,5)	57.888
D5	D(4,2,1,6)	-62.8222
D6	D(4,2,1,7)	176.4725
D7	D(8,3,2,1)	57.8382
D8	D(8,3,2,4)	183.2983
D9	D(9,3,2,1)	-62.8668
D10	D(9,3,2,4)	62.5933
D11	D(10,3,2,1)	176.4328
D12	D(10,3,2,4)	-58.1071
D13	D(11,4,2,1)	62.7113
D14	D(11,4,2,3)	-62.7395
D15	D(12,4,2,1)	-57.9987
D16	D(12,4,2,3)	176.5505
D17	D(13,4,2,1)	-176.5823
D18	D(13,4,2,3)	57.9669

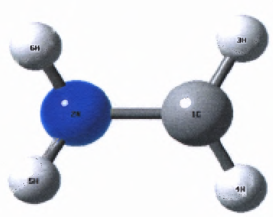
R1	R(2,1)	1.4552
R2	R(3,2)	1.4552
R3	R(4,2)	1.4551
R4	R(5,1)	1.0949
R5	R(6,1)	1.1084
R6	R(7,1)	1.0949
R7	R(8,3)	1.0949
R8	R(9,3)	1.1084
R9	R(10,3)	1.0949
R10	R(11,4)	1.1084
R11	R(12,4)	1.0948
R12	R(13,4)	1.0948
A1	A(1,2,3)	111.5318
A2	A(1,2,4)	111.5486
A3	A(3,2,4)	111.5316
A4	A(2,1,5)	109.794
A5	A(2,1,6)	113.3632
A6	A(5,1,6)	107.8684
A7	A(2,1,7)	109.7975
A8	A(5,1,7)	107.9919
A9	A(6,1,7)	107.8627
A10	A(2,3,8)	109.8017
A11	A(2,3,9)	113.3526
A12	A(8,3,9)	107.8657
A13	A(2,3,10)	109.799
A14	A(8,3,10)	107.9956
A15	A(9,3,10)	107.8636
A16	A(2,4,11)	113.3633
A17	A(2,4,12)	109.7769
A18	A(11,4,12)	107.8779
A19	A(2,4,13)	109.7924
A20	A(11,4,13)	107.8664
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 $CCNCO_2CC$

```
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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 $CCCNCO_2C$

```
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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_jCO_2CC

```
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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_jNCO_2CC

```
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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_jCNCO_2CC

```
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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 $CCNCO_2C_jC$

```
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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 $CCNCO_2CC_j$

```
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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 $CCCN_jCO_2C$

```
NAME (name of molecule)
CCCNjCO2C

COMMENTS:
from CCCNjCO2C.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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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 CCC_jNCO_2C

```
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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
```

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