New Jersey Institute of Technology
Digital Commons @ NJIT

Theses
Electronic Theses and Dissertations

Spring 5-31-2011

Thermochemical properties, bond energies and internal rotor potentials in methyl ethyl sulfide and oxygenated sulfur hydrocarbons intermediates for modeling its combustion and atmospheric chemistry

Guanghui Song
New Jersey Institute of Technology

Follow this and additional works at: https://digitalcommons.njit.edu/theses

Part of the Chemical Engineering Commons

Recommended Citation

Song, Guanghui, "Thermochemical properties, bond energies and internal rotor potentials in methyl ethyl sulfide and oxygenated sulfur hydrocarbons intermediates for modeling its combustion and atmospheric chemistry" (2011). *Theses*. 110.
https://digitalcommons.njit.edu/theses/110

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at Digital Commons @ NJIT. It has been accepted for inclusion in Theses by an authorized administrator of Digital Commons @ NJIT. For more information, please contact digitalcommons@njit.edu.

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a, user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use" that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select "Pages from: first page # to: last page #" on the print dialog screen

NJIT
New Jersey's Science &
Technology University

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

ABSTRACT

THERMOCHEMICAL PROPERTIES, BOND ENERGIES AND INTERNAL ROTOR POTENTIALS IN METHYL ETHYL SULFIDE AND OXYGENATED SULFUR HYDROCARBON INTERMEDIATES FOR MODELING COMBUSTION AND ATMOSPHERIC CHEMISTRY

by
Guanghui Song

Small (1 to 4 carbon) hydrocarbon sulfides and thiols are formed in the biosphere by microorganisms and subsequently emitted into the lithosphere, hydrosphere and atmosphere. In the atmosphere they are oxidized by photochemical and radical reactions to intermediate hydrocarbon and to sulfur oxides. The oxides of these sulfur compounds and the intermediates from the oxidation process are known to form aerosols that can counteract the global warming green house effect. Recent studies also suggest that some aerosols can also contribute to global warming. Sulfur oxides are also major contributors to acid rain as the results of the atmospheric chemistry oxidation reactions on sulfur hydrocarbons and H_2S involve SO_2 formation. It is of great value to understand the thermochemistry and the elementary reaction processes of these sulfur compounds in order to better model atmospheric chemistry and global warming. The oxidation chemistry is also of value in model development for improvement of combustion processes and pollutant reduction. This study determines the structures, internal rotor potentials, bond energies and thermochemical properties ($\Delta_f H^o$, S^o and Cp(T)) of methyl ethyl sulfide ($CH_3SCH_2CH_3$), a widely used sulfuric hydrocarbon, and its main partial oxidation products in the atmosphere (CH_3SCH_2CHO, CH_3CH_2SCHO and $CH_3SC(=O)CH_3$). At the same time their radicals after losing one H atom, and some of the main partial reaction intermediate molecules and their main radicals after loss of an H atom have also been studied. The molecular structure and H-molecule bond energy are determined using Density Functional B3LYP/6-31G (d,p) and B3LYP/6-31+G(2d,p) together with the higher level composite CBS-QB3. Enthalpies of formation (Hf) for stable species are calculated in the levels of B3LYP/6-31G (d,p), B3LYP/6-31+G(2d,p) and CBS-QB3 using work reactions that are presumed isodesmic. Internal rotation barriers have also been determined with some other DFT methods. Then, thermochemical parameters (S^o and Cp(T)) are determined with the help of the Hf values and the data of moments of inertia and frequencies from the CBS-QB3 output files.

THERMOCHEMICAL PROPERTIES, BOND ENERGIES AND INTERNAL ROTOR POTENTIALS IN METHYL ETHYL SULFIDE AND OXYGENATED SULFUR HYDROCARBONS INTERMEDIATES FOR MODELING ITS COMBUSTION AND ATMOSPHERIC CHEMISTRY

by
Guanghui Song

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

Otto H. York Department of
Chemical, Biological and Pharmaceutical Engineering

May 2011

Blank Page

APPROVAL PAGE

THERMOCHEMICAL PROPERTIES, BOND ENERGIES AND INTERNAL ROTOR POTENTIALS IN METHYL ETHYL SULFIDE AND OXYGENATED SULFUR HYDROCARBONS INTERMEDIATES FOR MODELING ITS COMBUSTION AND ATMOSPHERIC CHEMISTRY

Guanghui Song

Dr. Joseph W Bozzelli, Dissertation Advisor Date
Distinguished Professor of Chemistry and Environmental Science, NJIT
Adjunct Professor of Chemical, Biological& Pharmaceutical Engineering, NJIT

Dr. Reginald P Tomkins, Committee Member Date
Professor of Chemical, Biological& Pharmaceutical Engineering, NJIT

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

Dr. Rubik Asatryan, Committee Member Date
Research Professor of Chemistry and Environmental Science, NJIT

BIOGRAPHICAL SKETCH

Author: Guanghui Song

Degree: Master of Science

Date: May 2011

Undergraduate and Graduate Education:

- Master of Science in Chemical Engineering,
  New Jersey Institute of Technology, Newark, NJ, 2011

- Bachelor of Science in Chemical Engineering,
  Xiamen University, Xiamen, P. R. China, 2008

Major: Chemical Engineering

Work like you don’t need money,
Love like you’ve never been hurt,
Sing as if no one can hear you,
And dance like no one’s watching.
Anonymous

Other men live to eat, while I eat to live.
Socrates

We soon believe what we desire.
Chaucer

The darkest hour is that before the dawn.
Fuller

Living without an aim is like sailing without a compass.
J. Ruskin

ACKNOWLEDGMENT

The author acknowledges partial funding for this research from Army Research Office Grant W911NF0410120.

Then, the author wants to thank primarily for the informative and helpful guide from Prof. Joseph Bozzelli, together with the financial support from him.

At the same time, the author wants to thank Prof. Tamara Gund, Prof. Rubik Asatryran and Prof. Reginald P. Tomkins for serving on the Master Thesis Committee.

Among the committee members, the author wants to thank Prof. T. Gund for teaching the course of Advanced Organic Chemistry, which is about advanced organic structural chemistry and applications of computational chemistry and molecular orbits. Then there are great thanks to Prof. R. Tomkins for serving as the graduate study advisor of Chemical Engineering programme in the Otto H. York Department, and great thanks to Prof. Rubik A. for his technical and analytical support.

At last the author wants to thank a lot to help from all the other members in the same research group, they're Ms. Itsaso Auzmendi, Mr. Sumit Charaya, Ms. Yui Suarwee and Ms. Anjani Gunturu. Together with thanks to Dr. Larisa Krishtopa, the director of Material Characterization Lab in NJIT, for teaching all the required analytical ideas and skills while being in the lab course of Instrumental Analysis. The author also strongly wants to thank all spiritual energizing from the parents, and many of the friends.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF TABLES
(Continued)

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

Figures **Page**

CHAPTER 1

INTRODUCTION

1.1 Introduction

Atmospheric sulfur chemistry is important in climate change because both natural and anthropogenic emission of sulfur compounds result in formation of particulate in the atmosphere (aerosols) that reflect solar and absorb IR radiation; they also affect production of atmospheric haze, acid rain, and ozone depletion. [8, 12] These sulfur oxide particles may also act as condensation nuclei for water vapor and enhance global cloudiness. It is generally considered that sulfur particulate reflection of incoming light to the earth benefits (reduces) global warming [21]. The primary natural sources of sulfur are volcanic emissions for oxides and production by biological processes in environmental waters and by phytoplankton for the reduced sulfur species: sulfides disulfides and thiols.

Anthropogenic impact on the sulfur cycle is primarily through the production of sulfur dioxide (SO_2) from industry, such as burning coal and the internal combustion engine emissions. Sulfur dioxide can adsorb onto surfaces where it can be oxidized to sulfate in the soil, harm plants, undergo biological reactions involving reduction to sulfide, or oxidization to sulfate. [8] In the atmosphere it can be oxidized to sulfuric acid, a principal component of acid rain or adsorb on particulate. In the absence of major breakthrough in the combustion technology and coal conversion, atmospheric pollution and acid rains are likely to worsen. Acid rain is presently considered one of the ten more serious problems in the world environment [20].

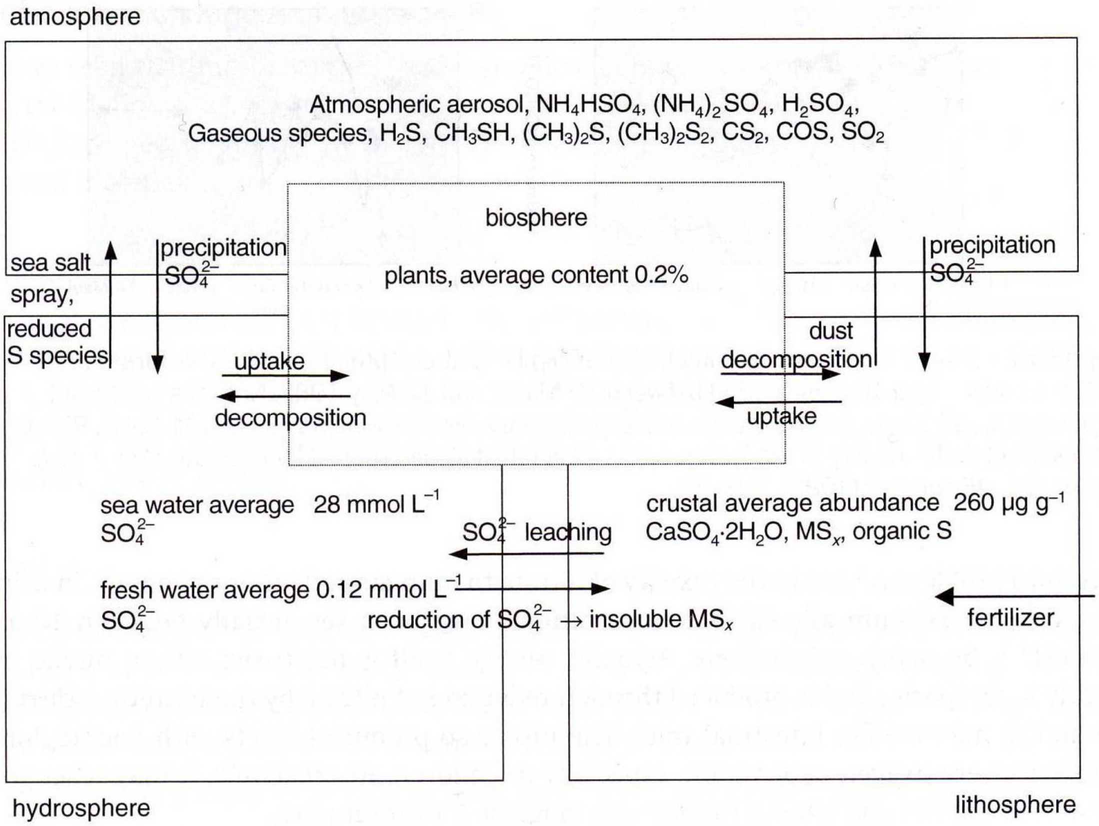


Figure 1.1 Sulfur cycle in the nature. [21]

These sulfur oxygen species in soils and environmental waters can serve as sources of oxygen to biological species, where the conversion to the more thermodynamically stable CO_2, provides an energy source for the biological species (micro organisms). This biological component of the sulfur cycle is further evidenced by the hydrogen, carbon and hydrocarbon sulfides, and corresponding thiols that are present at significant levels in natural gas wells. These sulfur species are not desirable for emission to the atmosphere and are treated (collected) by adsorption in amine solutions and either oxidized or combusted to form H_2SO_4 and SOx, or reacted to form solid sulfur, which is stored or land filled [17, 21].

Methyl Ethyl sulfide ($CH_3SCH_2CH_3$) is a widely used sulfuric compound. It's mainly used as an additive in the flavor agents. It tastes excellent. However, it's to some extent dangerous to the human body when overdosed, and it's harmful to the nature when released to the atmosphere. It's a volatile liquid at the standard state (T=298K and P=1atm). When released into the atmosphere, it mainly undergoes photochemical radical reaction with O_2, which is a partial oxidation reaction. A study to its partial radical oxidation in the atmosphere is required, to make sure it's able to be oxidized naturally and without generating SO_2. Fei Jin and Bozzelli, and Zhong, Fisher, Zhu and Bozzelli have developed the thermochemistry and kinetics for the oxidation reactions of Dimethyl Sulfide and Diethyl Sulfide, respectively [8, 11, 12]. Learning from their work, the partial oxidation of methyl ethyl sulfide in the atmosphere is proposed to generate the intermediate products of CH_3SCH_2CHO, CH_3CH_2SCHO and $CH_3SC(=O)CH_3$, and the proposed intermediates of partial oxidation are $HOOCH_2SCH_2CH_3$, $CH_3SCH(OOH)CH_3$ and $CH_3SCH_2CH_2OOH$, sometimes also CH_3SCH_2OH, $CH_3CH_2SCH_2OH$, $CH_3S(=O)CH_2OH$ and $CH_3S(=O)CH(OH)CH_3$. These products and intermediates in the atmosphere are also probable intermediates of the combustion reaction of $CH_3SCH_2CH_3$. As a result, the thermochemistry of $CH_3SCH_2CH_3$, and its proposed partial particle oxidation products and intermediates and products is of value.

1.2 Objective

Density functional theory based calculations along with higher level ab initio methods are performed on a series of sulfuric hydrocarbon compounds containing one sulfur atom and one or two oxygen atoms in each molecule. The B3LYP/6-31G(d,p) and B3LYP/6-31+G(2d,p) calculation levels have been applied in Gaussian 98, and composite CBS-QB3 level has been performed in Gaussian 03 [13]. The geometric structures, enthalpies of formation, H—X(X=C,O) bond energies, frequencies and moments of inertia, internal rotational potentials and the entropy and heat capacity values at 298K and 1atm have been studied on the targeted stable molecules. The carbon or oxygen centered radicals, resulting from loss of H atoms are also studied in order to determine bond energies. These reliable and accessible thermochemical data are universally accepted as needed for understanding the reactions and stability of chemical species [18, 19].

In Chapter 2, the targets are the proposed atmospheric partial oxidation products: sulfide aldehydes and ketones. The target molecules and their radicals are: CH_3SCH_2CHO with the radicals of CH_2jSCH_2CHO, $CH_3SCHjCHO$ and $CH_3SCH_2Cj{=}O$; CH_3CH_2SCHO with the radicals of CH_2jCH_2SCHO, CH3CHjSCHO and $CH_3CH_2SCj{=}O$; and $CH_3SC({=}O)CH_3$ with the radicals of $CH_2jSC({=}O)CH_3$ and $CH_3SC({=}O)CH_2j$.

Then in Chapter 3, at first the targets to study are methyl ethyl sulfide ($CH_3SCH_2CH_3$) and its radicals after one H atom is abstracted from the different carbon atoms: $CH_2jSCH_2CH_3$, $CH_3SCHjCH_3$ and $CH_3SCH_2CH_2j$. Then the targets are the proposed intermediates during reactions of oxygen molecule O_2 with each of the three of methyl ethyl sulfide’s carbon radicals. The main intermediates from the radical reactions with O_2, together with their new intermediate radicals are formed in some isomerization reactions, and each of them contains a hydrogen peroxide group attached to a carbon atom. These include: $HOOCH_2SCH_2CH_3$ (with the radicals of $jOOCH_2SCH_2CH_3$, $HOOCH_2SCHjCH_3$ and $HOOCH_2SCH_2CH_2j$), $CH_3SCH(OOH)CH_3$ (with the radicals of $CH_2jSCH(OOH)CH_3$, $CH_3SCH(OOj)CH_3$ and $CH_3SCH(OOH)CH_2j$) and $CH_3SCH_2CH_2OOH$ (with the radicals of $CH_2jSCH_2CH_2OOH$, $CH_3SCHjCH_2OOH$ and $CH_3SCH_2CH_2OOj$).

In Chapter 3 the stable molecules of CH_3SCH_2OH, $CH_3CH_2SCH_2OH$, $CH_3S(=O)CH_2OH$ and $CH_3S(=O)CH(OH)CH_3$ have also been studied, as they're also some common intermediates of methyl ethyl sulfide's radical reaction with O_2.

CHAPTER 2

STRUCTURES, THERMOCHEMISTRY, INTERNAL ROTOR POTENTIALS AND CARBON – HYDROGEN BOND ENERGIES IN SULFIDE ALDEHYDES AND KETONES AS PRODUCTS OF ATMOSPHERIC PARTIAL OXIDATION

Overview

The structure and thermochemical parameters ($\Delta_f H^o(298)$, S^o and Cp(T)), internal rotor potentials and carbon--hydrogen bond energies for some ethyl methyl sulfide partial oxidation were studied to prepare for kinetic studies on the oxidation of ethyl methyl sulfide under atmospheric and combustion conditions. The thermochemical and structural properties were determined using computational chemistry.

2.1 Calculation Methods

The structural and thermochemical parameters of CH_3SCH_2CHO, CH_3CH_2SCHO and $CH_3SC(=O)CH_3$ and their radicals are based on the Density Functional Theory (DFT) and composite ab initio levels using Gaussian 98. Computation levels include B3LYP/6-31G(d,p) and B3LYP/6-31+G(2d,p) DFT methods along with the higher level, composite CBS-QB3 method from the Gaussian 03 code [10]. Enthalpies of formation for stable species are calculated using the total energies (298 K) at each level with work reactions that are close to isodesmic in most cases. Isodesmic reactions conserve the number and type of bonds on both sides of an equation. The use of a work reaction with similar bond environments on both sides of the equation results in a cancellation of calculation error and improves the accuracy for energy analysis. Three to six work reactions are utilized and results are presented for each calculation level and each reaction. Average values over the three calculation methods for each work reaction, and separately the average values over the work reactions for each calculation method are presented. The average value over the work reactions at the CBS-QB3 level are recommended $\Delta_f H^o(298)$, as this method has the highest accuracy. $\Delta_f H^o(298)$ data are reported for each species [8, 18, 19].

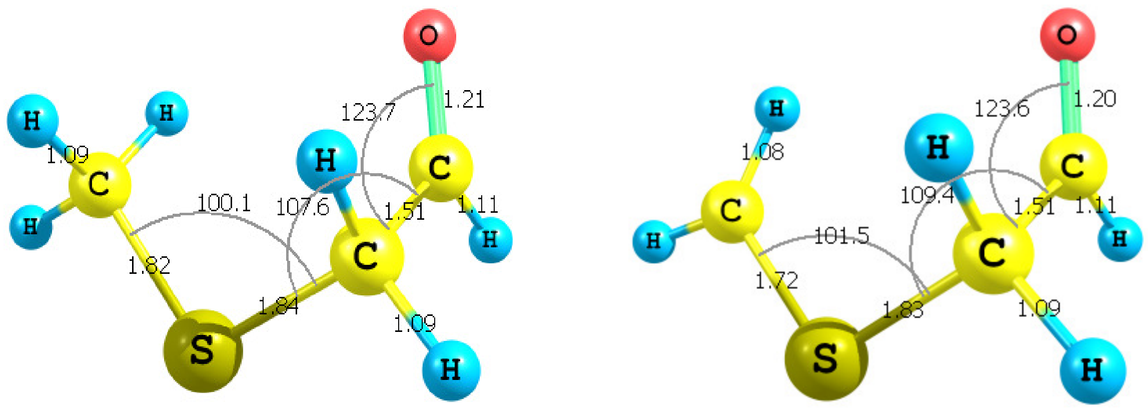
The Entropy S°(T=298K) and Cp°(T, T=298-1500K) were calculated using the "SMCPS" [24] (Statistical Mechanics for Heat Capacity and Entropy Cp and S) program. Information in the CBS-QB3 output file are to be used to the inertias and frequencies to input in the SMCPS input files, and to get the most stable structures of the species [16, 18]. And torsion frequencies are used for internal rotor contribution.

2.2 Results and Discussion

2.2.1 Structures

Scans of internal rotor energy versus dihedral angle have been performed at the B3LYP/6-31G(d,p) level for each molecule and radical to identify the lowest energy conformer. The lowest energy for each scan is obtained and that energy used as the structure for the start of the next internal rotor. When a lower energy conformer is found in a subsequent scan then that is selected and all previous scans are repeated until the lowest energy conformer is found. The optimized low energy structures are illustrated in Figure 2.4-2.14.

Figure 2.1 shows the lowest energy configurations of the stable CH_3SCH_2CHO molecule and its three radicals: $CjH_2SCH_2CH^*O$, $CH_3SCjHCH^*O$ and $CH_3SCH_2Cj^*O$ with the bond distances and the angles illustrated. The dihedral angles for C-S-C-C and S-C-C=O, are described directly below the Figure.

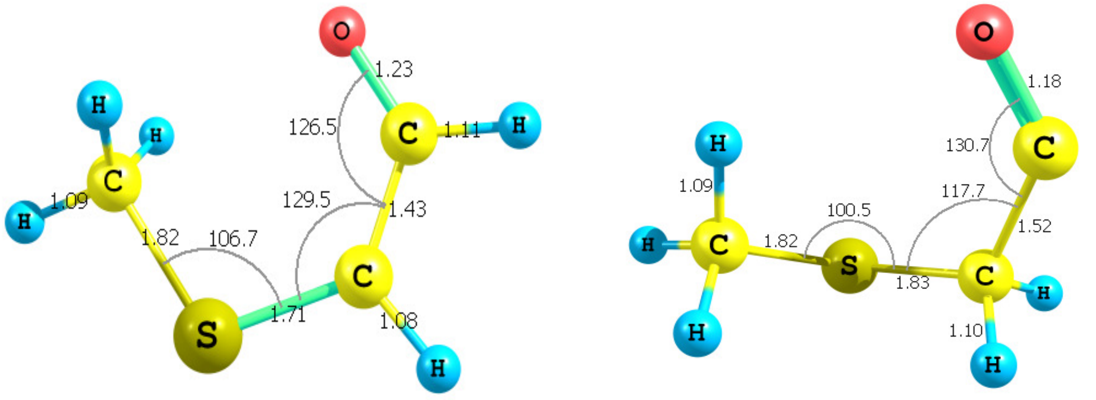


(a) CH_3SCH_2CHO

C-S-C-C =-70.3˚   S-C-C=O =102.3˚

(b) CH_2jSCH_2CHO

C-S-C-C =-66.9˚   S-C-C=O =109.0˚



(c) $CH_3SCHjCHO$

C-S-C-C =0.0˚   S-C-C=O =0.0˚

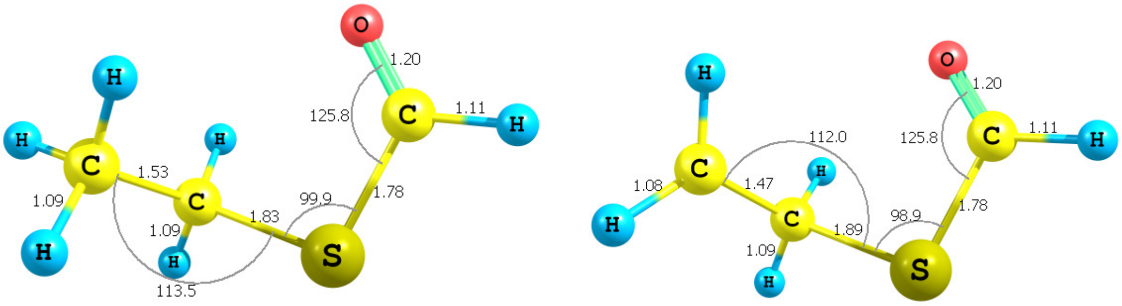
(d) $CH_3SCH_2Cj{=}O$

C-S-C-C =-63.7˚   S-C-C=O =12.2˚

Figure 2.1 Optimized structures of CH_3SCH_2CHO, CH_2jSCH_2CHO, $CH_3SCHjCHO$ and CH_3SCH_2CjO at CBS-QB3 level (Bond distances in Å; Bond Angles in º).

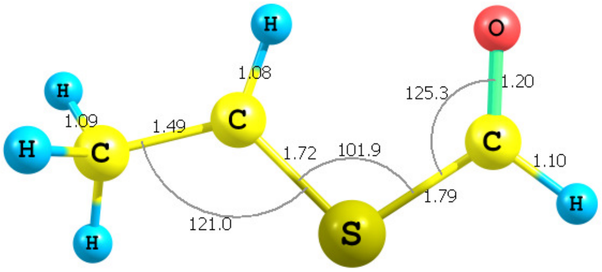
First, in the stable CH_3SCH_2CHO molecule, all the C--H bonds are about 1.1A°, both bonds of C—SCC*O and CS—CC*O are about 1.8A°, CSC—C*O is 1.51A° and CSCC(==)O is 1.21A°. And the C—S—CC*O angle is 100.1 º, the CS—C—C*O angle is 107.6º, the CSC—C==O angle is 123.7º. Then, for the radicals, when compared to the parent: 1) in CH_2jSCH_2CHO, C—SCC*O has shortened evidently to 1.72A°; 2)in $CH_3SCHjCHO$, C—S—CC*O has increased to 106.7°, CS—C—C*O has increased to

129.5°, and CS—CC*O has shortened evidently to 1.71A°, CSC—C*O has decreased to 1.43A°; 3)in CH_3SCH_2CjO, CS—C—C*O has increased evidently to 117.7° and CSC—C==O has increased to 130.7 °, but there is no evident change to each bond compared to the parent molecule.

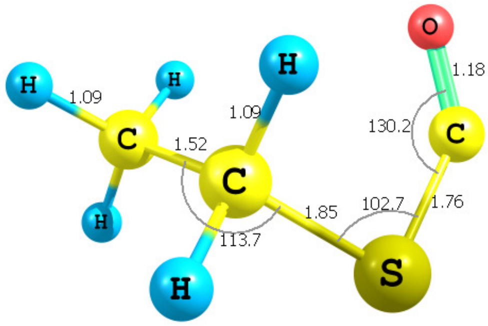


(a) CH_3CH_2SCHO
C-C-S-C =-84.3° C-S-C=O =-0.5°

(b) CH_2jCH2SCHO C-C-S-C =-81.5°
C-S-C=O =-0.6°



(c) $CH_3CHjSCHO$ C-C-S-C =-174.3° C-S-C=O =0.9°

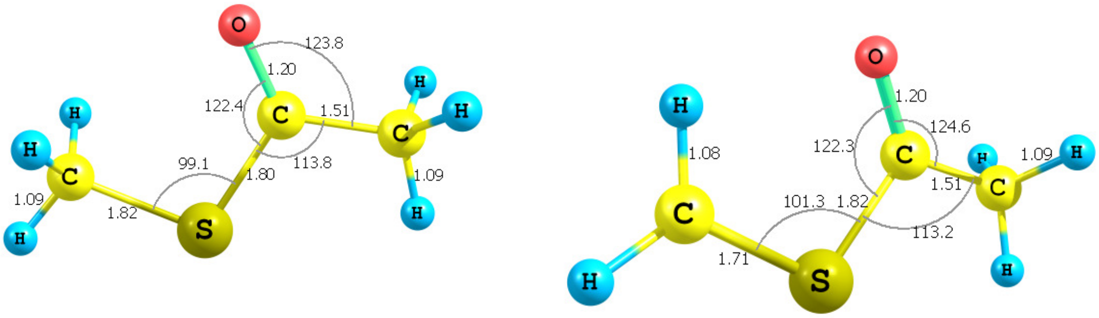


(d) $CH_3CH_2SCj{*}O$ C-C-S-C =77.3° C-S-C=O =0.1°

Figure 2.2 Optimized structures of CH_3CH_2SCHO, CH_2jCH_2SCHO, $CH_3CHjSCHO$ and CH_3CH_2SCjO at CBS-QB3 level (Bond distances in Å; Bond Angles in °).

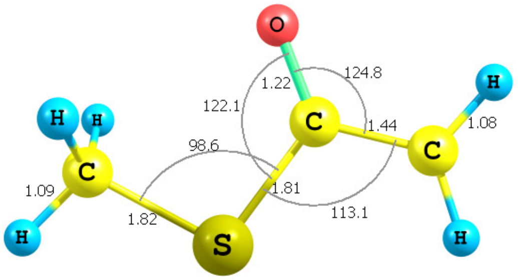
Figure 2.2 shows the four lowest energy configurations of the stable CH_3CH_2SCHO molecule and its three radicals CjH_2CH_2SCH*O $CH_3CjHSCH*O$, CH_3CH_2SCj*O with bond distances and angles in the figure. The dihedral angles are below the figure of each molecule and radical in the figure.

The stable CH_3CH_2SCHO molecule has all C--H bond lengths also about 1.1A°, C—CSC*O is 1.53A°, CC—SC*O is 1.83A°, CCS—C*O is 1.78A° and CCSC==O is 1.20A°. And the angle of C—C—SC*O is 113.5°, CC--S--C*O is 99.9° and CCS—C==O is 125.8°. Then, for the radicals, when compared to the parent: 1) in CH_2jCH_2SCHO, CC—SC*O has increased evidently to 1.89A°, C—C—SC*O has decreased to 112.0°; 2) in $CH_3CHjSCHO$, CC—SC*O has shortened to 1.72A°, C—C—SC*O has increased to 121.0° and CC—S—C*O has increased to 101.9°; 3) in CH_3CH_2SCjO, CC--SC*O has increased to 1.85A°, CC—S—C*O has increased to 102.7° and CCS—C==O has increased to 130.2°.



(a) $CH_3SC(=O)CH_3$ C-S-C=O =0.0˚ C-S-C-C =180.0˚

(b) $CH_2jSC(=O)CH_3$ C-S-C=O =0.0˚ C-S-C-C =-180.0˚



(c) $CH_3SC(=O)CH_2j$ C-S-C=O =0˚ C-S-C-C =180.0˚

Figure 2.3 Optimized structures of $CH_3SC(=O)CH_3$, $CH_2jSC(=O)CH_3$, and $CH_3SC(=O)CH_2j$ at CBS-QB3 level (Bond distances in Å; Bond Angles in º).

Figure 2.3 shows the three lowest energy configurations of the stable $CH_3SC(=O)CH_3$ molecule and its two radicals with bond distances and angles. The dihedral angles are listed directly below each figure.

In the stable $CH_3SC(=O)CH_3$, all the C—H bonds of are still about 1.1A°, both C—SC(*O)C and CS—C(*O)C are also about 1.8A°, CSC(==O)C is also about 1.2A°, CSC(*O)—C is 1.51A°. And the angle of C—S—C(*O)C is 99.1°, CS—C(==O)C is 122.4° and CSC(==O)—C is 123.8°. Then, for the radicals: 1) in $CH_2jSC(=O)CH_3$, C—SC(*O)C has shortened to 1.71A°, and C—S—C(*O)C has increased to 101.3°; 2) in $CH_3SC(=O)CH_2j$, CSC(==O)—C has decreased to 1.44A°, but there is no evident change in each bond angle.

After a hydrogen atom (H) is removed from a carbon atom, the positive charge on the carbon atom is less neutralized by loss of the shared H atom electron. Also, there has an unpaired electron on the carbon that interacts with neighboring atoms. Therefore, the electrostatic interaction between this carbon and its neighbor atoms increases. In the case of the C—S bonds and C—H bonds, the bond lengths are reduced, this is true especially as the unpaired electron on the carbon interacts with the unbonded electrons on the neighboring sulfur atom.

Departure of the H atom from the carbon atoms neighboring to the sulfur atom, like CSC(—H)C*O and H—CSC(*O)C, leads to formation of a partial double bond (π bond) between the sulfur atom and the carbon atom: CS-.CC=O and C-.SC(=O)C. This also effects the double bond between the oxygen and carbon atom in the carbonyl group C(=O), where this bond is often lengthened slightly. This is also brought about by the interaction between the unpaired electron on the radical site carbon and the unbounded electrons on the neighboring sulfur atom.

2.2.2 Heats of Formation and Enthalpies of Reaction

There are several methods that are used for estimating the enthalpy of formation of a molecule when T=298K (ΔH^o_{f298}):

i) Enthalpy of Atomization [22]. It's mainly used on gaseous molecules. Each work reaction follows the atom balance rule, using CH_3SCH_2CHO as an example:

$CH_3SCH_2CHO = 3C + 6H + S + O$

It's based completely on the enthalpy change before and after separating all the atoms decomposing a chemical substance into single atoms. It equals the sum of the dissociation energy of all bonds within the molecule. Standard atomization enthalpy equals the enthalpy change when 1 mol of atoms in the gas phase is formed from its element in its defined physical state under T=298.15K and P=1atm [22]. As all bonds in the compound molecule are broken into atoms and none are formed, the atomization value is always positive.

ii) Enthalpy of formation [23]. It's the change of enthalpy that accompanied the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states (T=298.15K and P=1atm) [23]. Also, use a work reaction for CH_3SCH_2CHO as an example:

$CH_3SCH_2CHO = 3C(s) + 3H_2 + S(s) + 1/2O_2$

All elements in their standard states (such as oxygen gas, hydrogen gas, and solid carbon in the form of graphite and solid sulfur) have a standard enthalpy of formation of zero, and there is no change involved in their formation.

iii) This is the use of work reactions with bond and hybridization balance. Example work reactions are shown as follow:

$CH_3SCH_2CHO + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_3CH_2CHO$

$CH_3SCH_2CHO + CH_4 \rightarrow CH_3SCH_3 + CH_3CHO$

For each work reaction, similar bond environments are required in the bonds of the reactants and products. The following example shows how each work reaction works:

$CH_3SCH_2CHO + CH_4 \rightarrow CH_3SCH_3 + CH_3CHO$

Unknown -17.8 -9.0 -40.9 $\Delta H_f°_{298}$ kcal mol^{-1}

(Reference Species values from Literature)

$\Delta H°\text{rxn},_{298} = \Delta H_f°_{298}\ [CH_3SCH_3] + \Delta H_f°_{298}\ [CH_3CHO]$

$– \Delta H_f°_{298}$ [CH_4] – $\Delta H_f°_{298}$ [CH_3SCH_2CHO]

$\Delta H°$rxn,$_{298}$[CH_3SCH_2CHO] = 3.6 kcal mol^{-1}(This calculation)

(This is calculated with DFT method)

using ΔHrxn = $\Sigma\Delta_fH^o(298)$ products – Σ $\Delta_fH^o(298)$ reactants

3.6 = -9.0 + (-40.9) – (-17.8) – (CH_3SCH_2CHO) kcal mol^{-1}

Find $\Delta H_f°_{298}$ of CH_3SCH_2CHO = -35.6kcal/mol

In order to improve precision, several different work reactions were applied for each targeted species, this provides statistics and validation for the $\Delta_fH^o(298)$ obtained.

In determining enthalpy of formation of a molecule, methods i), ii) and iii) only calculate one species each time, but error cancellation in method iii) results in higher accuracy. Although for method iii) it initially requires accurate Hf values of all the reference species beyond the target molecule, methods i) and ii) suffer from low accuracy due to lack of effective error cancellation method. As a result method iii) is applied to calculate enthalpies of formation for all the targeted species.

Enthalpies of formation $\Delta_fH^o(298)$ of the target parent and radical intermediates have been determined using calculated $\Delta_fH^o(298)$ values for each species, then calculating the ΔHreaction at 298 K, and then using the known literature values for the three reference molecules in the work reaction and the calculated ΔHrxn find $\Delta_fH^o(298)$ of the target. The standard enthalpies of formation of the reference species at 298K used in the work reactions are summarized in Table 2.1. For radical species, the work reactions included the parent molecule and used the enthalpy value of the parent determined in this study as a reference.

$\Delta H_{rxn(298)} = \sum H_f$ products - $\sum H_f$ reactants

The work reactions in Table 2.2 are used to calculate the heat of reaction and enthalpies of formation for CH_3SCH_2CHO, CH_3CH_2SCHO, $CH_3SC(=O)CH_3$ parent molecules and their radicals formed after removal of one H atom. The enthalpy calculations and the reported values are based on the lowest energy conformer.

Table 2.2 lists the calculated enthalpies of reaction from the five corresponding work reactions for each molecule, and their radicals formed after loss of one H atom from a carbon atom. There are five different work reactions utilized in each species, and results are presented for each calculation level and each reaction. Average values over the three calculation methods for each work reaction, and separately the average values over the work reactions for each calculation method are presented. The average value over the work reactions at the CBS-QB3 level are recommended $\Delta_f H^o(298)$, as this method has the highest accuracy. $\Delta_f H^o(298)$ data are reported for each species.

The resultant CBS-QB3 Hf values from the work reactions in Table 2.2 are applied when studying the C—H bond energies. These are also the values used in reporting the thermochemical properties in the following sections.

Information in the CBS-QB3 output files are used to get the inertias and frequencies to input in the SMCPS input files, and the most stable structures of the species.

It’s evident that the enthalpies of formation for each radical are much higher than those of their parent molecules. Their enthalpy values, relative to each other, demonstrate the relative ease of formation, and their relative stability. The higher the enthalpy, the less stable the radical and usually the more difficult to form.

Table 2.1 Standard Enthalpies of Formation of Reference Species at 298.15 K.

Species	**$\Delta H_f{}^o{}_{298}$(kcal mol^{-1})**	**References**
CH_4	-17.83	[14]
CH_3CH_3	-20.04	[14]
CH_3SCH_3	-8.96	[11]
CH_3CHO	-40.9	[14]
CH_3OH	-48.02	[14]
$CH_3C(=O)OH$	-103.5	[14]
CH_3OCH_3	-43.99	[16]
$CH_3C(=O)OCH_3$	-98	[16]
$CH_3C(=O)CH_3$	-51.56	[17]
CH_3SH	-5.47	[16]
CH_2jSH	37.7	[16]
$CH_3CH_2CH_3$	-24.82	[14]
$CH_2jCH_2CH_3$	23.67	[16]
CH_2jCH_3	28.4	[12]
CH_2jSCH_3	32.66	[12]
CH_3CH_2OH	-56.23	[14]
CH_2jCH_2OH	-7.2	[19]
CH_3CH_2CHO	-45.18	[19]
$CH_3CH_2Cj=O$	-7.45	[19]
$CH_3CHjCHO$	-7.1	[19]
$CH_2jCH2CHO$	5.1	[19]
CH_2jCHO	3.6	[19]
$CH_3Cj=O$	-3	[19]

Table 2.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation (ΔH^o_{f298}) of CH_3SCH_2CHO, CH_3CH_2SCHO, $CH_3SC(=O)CH_3$ and Their Radicals (Units: kcal/mol).

$\Delta H_f^o{}_{298}$(kcal mol^{-1})	**B3LYP**		**CBS-QB3**	**Average**
Work Reactions	**6-31G(d,p)**	**6-31+G(2d,p)**		
CH_3SCH_2CHO				
$CH_3SCH_2CHO+CH_3CH_3 \rightarrow CH_3SCH_3+CH_3CH_2CHO$	-35.1	-35.0	-35.6	-35.3
$CH_3SCH_2CHO+CH_4 \rightarrow CH_3SCH_3+CH_3CHO$	-33.9	-33.8	-35.6	-34.4
$CH_3SCH_2CHO+CH_3OH \rightarrow CH_3SCH_3+CH_3CO2H$	-31.2	-33.9	-34.9	-33.4
$CH_3SCH_2CHO+CH_3OCH_3 \rightarrow CH_3SCH_3+CH_3CO2CH_3$	-32.1	-33.9	-34.2	-33.4
$CH_3SCH_2CHO+CH_3CH_3 \rightarrow CH_3SCH_3+CH_3C(=O)CH_3$	-33.7	-33.6	-34.2	-33.8
Average	-33.2	-34.1	**-34.9**	-34.1
Hf= -34.9, use the average value of the CBS-QB3 level				
CH_2jSCH_2CHO				
$CH_2jSCH_2CHO+CH_3SH \rightarrow CH_3SCH_2CHO+CH_2jSH$	8.9	9.1	9.8	9.3
$CH_2jSCH_2CHO+CH_3CH_2CH_3 \rightarrow CH_3SCH_2CHO+CH_2jCH_2CH_3$	8.9	8.4	7.7	8.3
$CH_2jSCH_2CHO+CH_3CH_3 \rightarrow CH_3SCH_2CHO+CH_2jCH_3$	9.1	8.5	8.3	8.6
$CH_2jSCH_2CHO+ CH_3SCH3 \rightarrow CH_3SCH_2CHO+ CH_2jSCH_3$	8.6	9.1	8.9	8.9
$CH_2jSCH_2CHO+CH_3CH_2OH \rightarrow CH_3SCH_2CHO+CH_2jCH_2OH$	8.1	7.7	7.4	7.7
Average	8.7	8.6	**8.4**	8.6
Hf=8.4, use the average value of the CBS-QB3 level				
$CH_3SCHjCHO$				
$CH_3SCHjCHO+CH_3CH_2CHO \rightarrow CH_3SCH_2CHO+CH_3CH_2CjO$	-4.1	-3.8	-2.6	-3.5
$CH_3SCHjCHO+CH_3CH_2CHO \rightarrow CH_3SCH_2CHO+CH_3CHjCHO$	-3.2	-3.3	-3.2	-3.2
$CH_3SCHjCHO+CH_3CH_2CHO \rightarrow CH_3SCH_2CHO+CH_2jCH_2CHO$	-5.6	-5.3	-2.6	-4.5
$CH_3SCHjCHO+ CH_3CHO \rightarrow CH_3SCH_2CHO+ CH_2jCHO$	-4.8	-4.9	-3.4	-4.4
$CH_3SCHjCHO+ CH_3CHO \rightarrow CH_3SCH_2CHO+ CH_3CjO$	-6.3	-5.7	-4.5	-5.5
Average	-4.8	-4.6	**-3.3**	-4.2
Hf= -3.3, use the average value of the CBS-QB3 level				
CH_3SCH_2CjO				
$CH_3SCH_2CjO+CH_3CH_2CHO \rightarrow CH_3SCH_2CHO+CH_3CH_2CjO$	4.8	5.5	5.4	5.2
$CH_3SCH_2CjO+CH_3CH_2CHO \rightarrow CH_3SCH_2CHO+CH_3CHjCHO$	5.7	6.0	4.8	5.5
$CH_3SCH_2CjO+CH_3CH_2CHO \rightarrow CH_3SCH_2CHO+CH_2jCH_2CHO$	3.3	4.0	5.5	4.3
$CH_3SCH_2CjO+ CH_3CHO \rightarrow CH_3SCH_2CHO+ CH_2jCHO$	4.1	4.4	4.6	4.4
$CH_3SCH_2CjO+ CH_3CHO \rightarrow CH_3SCH_2CHO+ CH_3CjO$	2.6	3.6	3.5	3.3
Average	4.1	4.7	**4.8**	4.5
Hf=4.8, use the average value of the CBS-QB3 level				
CH_3CH_2SCHO				
$CH_3CH_2SCHO+CH_3CH_3 \rightarrow CH_3SCH_3+CH_3CH_2CHO$	-44.5	-44.1	-43.7	-44.1
$CH_3CH_2SCHO+CH_4 \rightarrow CH_3SCH_3+CH_3CHO$	-43.3	-42.9	-43.7	-43.3
$CH_3CH_2SCHO+CH_3OH \rightarrow CH_3SCH_3+CH_3CO2H$	-40.6	-43.0	-43.0	-42.2
$CH_3CH_2SCHO+CH_3OCH_3 \rightarrow CH_3SCH_3+CH_3CO2CH_3$	-41.5	-43.0	-42.3	-42.2
$CH_3CH_2SCHO+CH_3CH_3 \rightarrow CH_3SCH_3+CH_3C(=O)CH_3$	-43.1	-42.7	-42.3	-42.7
Average	-42.6	-43.2	**-43.0**	-42.9
Hf=-43.0, use the average value of the CBS-QB3 level				
CH_2jCH_2SCHO				
$CH_2jCH_2SCHO+CH_3SH \rightarrow CH_3CH_2SCHO +CH_2jSH$	4.2	5.0	6.9	5.4
$CH_2jCH_2SCHO+CH_3CH_2CH_3 \rightarrow CH_3CH_2SCHO +CH_2jCH_2CH_3$	4.1	4.3	4.7	4.4
$CH_2jCH_2SCHO+CH_3CH_3 \rightarrow CH_3CH_2SCHO +CH_2jCH_3$	4.3	4.4	5.3	4.7
$CH_2jCH_2SCHO+CH_3SCH_3 \rightarrow CH_3CH_2SCHO + CH_2jSCH_3$	3.9	5.0	5.9	4.9
$CH_2jCH_2SCHO+CH_3CH_2OH \rightarrow CH_3CH_2SCHO +CH_2jCH_2OH$	3.3	3.6	4.4	3.8
Average	3.9	4.5	**5.4**	4.6
Hf=5.4, use the average value of the CBS-QB3 level				
$CH_3CHjSCHO$				
$CH_3CHjSCHO+ CH_3CH_2CHO \rightarrow CH_3CH_2SCHO + CH_3CH_2CjO$	2.5	1.4	1.5	1.8
$CH_3CHjSCHO+ CH_3CH_2CHO \rightarrow CH_3CH_2SCHO + CH_3CHjCHO$	3.4	2.0	1.0	2.1
$CH_3CHjSCHO+ CH_3CH_2CHO \rightarrow CH_3CH_2SCHO + CH_2jCH_2CHO$	1.0	0.0	1.6	0.9
$CH_3CHjSCHO+ CH_3CHO \rightarrow CH_3CH_2SCHO + CH_2jCHO$	1.8	0.4	0.7	1.0
$CH_3CHjSCHO+ CH_3CHO \rightarrow CH_3CH_2SCHO + CH_3CjO$	0.3	-0.4	-0.3	-0.2
Average	1.8	0.7	**0.9**	1.1
Hf=0.9, use the average value of the CBS-QB3 level				

Table 2.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation (ΔH^o_{f298}) of CH_3SCH_2CHO, CH_3CH_2SCHO, $CH_3SC(=O)CH_3$ and Their Radicals (Units: kcal/mol).
(Continued)

$\Delta H_f{}^o{}_{298}$(kcal mol^{-1})	**B3LYP**		**CBS-QB3**	**Average**
Work Reactions	**6-31G(d,p)**	**6-31+G(2d,p)**		
CH_3CH_2SCjO				
$CH_3CH_2SCjO + CH_3CH_2CHO \rightarrow CH_3CH_2SCHO + CH_3CH_2CjO$	-4.1	-4.4	-4.4	-4.3
$CH_3CH_2SCjO + CH_3CH_2CHO \rightarrow CH_3CH_2SCHO + CH_3CHjCHO$	-3.2	-3.9	-5.0	-4.0
$CH_3CH_2SCjO + CH_3CH_2CHO \rightarrow CH_3CH_2SCHO + CH_2jCH_2CHO$	-5.6	-5.8	-4.4	-5.3
$CH_3CH_2SCjO + CH_3CHO \rightarrow CH_3CH_2SCHO + CH_2jCHO$	-4.8	-5.4	-5.3	-5.2
$CH_3CH_2SCjO + CH_3CHO \rightarrow CH_3CH_2SCHO + CH_3CjO$	-6.3	-6.2	-6.3	-6.3
Average	-4.8	-5.1	**-5.1**	-5.0
Hf=-5.1, use the average value of the CBS-QB3 level				
$CH_3SC(=O)CH_3$				
$CH_3SC(=O)CH_3 + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_3CH_2CHO$	-51.1	-50.8	-50.8	-50.9
$CH_3SC(=O)CH_3 + CH_4 \rightarrow CH_3SCH_3 + CH_3CHO$	-49.8	-49.5	-50.8	-50.0
$CH_3SC(=O)CH_3 + CH_3OH \rightarrow CH_3SCH_3 + CH_3CO2H$	-47.2	-49.6	-50.1	-49.0
$CH_3SC(=O)CH_3 + CH_3OCH_3 \rightarrow CH_3SCH_3 + CH_3CO2CH_3$	-48.1	-49.6	-49.4	-49.0
$CH_3SC(=O)CH_3 + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_3C(=O)CH_3$	-49.6	-49.3	-49.4	-49.5
Average	-49.1	-49.8	**-50.1**	-49.7
Hf=-50.1, use the average value of the CBS-QB3 level				
$CH_2jSC(=O)CH_3$				
$CH_2jSC(=O)CH_3 + CH_3SH \rightarrow CH_3SC(=O)CH_3 + CH_2jSH$	-6.3	-6.0	-4.3	-5.5
$CH_2jSC(=O)CH_3 + CH_3CH_2CH_3 \rightarrow CH_3SC(=O)CH_3 + CH_2jCH_2CH_3$	-6.3	-6.8	-6.4	-6.5
$CH_2jSC(=O)CH_3 + CH_3CH_3 \rightarrow CH_3SC(=O)CH_3 + CH_2jCH_3$	-6.2	-6.7	-5.8	-6.2
$CH_2jSC(=O)CH_3 + CH_3SCH_3 \rightarrow CH_3SC(=O)CH_3 + CH_2jSCH_3$	-6.6	-6.1	-5.2	-6.0
$CH_2jSC(=O)CH_3 + CH_3CH_2OH \rightarrow CH_3SC(=O)CH_3 + CH_2jCH_2OH$	-7.1	-7.5	-6.7	-7.1
Average	-6.5	-6.6	**-5.7**	-6.3
Hf=-5.7, use the average value of the CBS-QB3 level				
$CH_3SC(=O)CH_2j$				
$CH_3SC(=O)CH_2j + CH_3CH_2CHO \rightarrow CH_3SC(=O)CH_3 + CH_3CH_2CjO$	-3.3	-3.4	-2.9	-3.2
$CH_3SC(=O)CH_2j + CH_3CH_2CHO \rightarrow CH_3SC(=O)CH_3 + CH_3CHjCHO$	-2.4	-2.9	-3.5	-2.9
$CH_3SC(=O)CH_2j + CH_3CH_2CHO \rightarrow CH_3SC(=O)CH_3 + CH_2jCH_2CHO$	-4.8	-4.8	-2.9	-4.2
$CH_3SC(=O)CH_2j + CH_3CHO \rightarrow CH_3SC(=O)CH_3 + CH_2jCHO$	-4.0	-4.4	-3.7	-4.1
$CH_3SC(=O)CH_2j + CH_3CHO \rightarrow CH_3SC(=O)CH_3 + CH_3CjO$	-5.5	-5.2	-4.8	-5.2
Average	-4.0	-4.1	**-3.5**	-3.9
Hf=-3.5, use the average value of the CBS-QB3 level				

2.2.3 C—H Bond Energies

Bond energies corresponding to the loss of an H atom from each of the three carbon atoms on the three parent molecules are reported at 298 K and 1 atm. The calculation are illustrated in Table 2.2 above where the radical $\Delta_f H^o(298)$ value is obtained from five work reactions. Bond energies for the formation of radicals reported at 298 K are calculated from the absolute ΔH^o_{f298} values of the parent molecules and radicals are from the average CBS-QB3 level calculations. The work reactions here use the corresponding $\Delta_f H^o(298)$ of the radical and the parent and that of the hydrogen atom, 52.1 kcal mol^{-1}. The C—H bond energies of the parent molecules are summarized in Table 2.3. The ΔHrxn of the reaction below is used to define the bond energy:

$$\Delta_f H^o(298)\text{ Parent} = \Delta_f H^o(298)\text{ Radical} + \text{H atom } (52.1)$$

The bond energies of H—CH_2SCH_2CHO, CH_3SCH(--H)CHO and CH_3SCH_2C(=O)--H are calculated using the reactions below:

$CH_3SCH_2CHO \rightarrow H\bullet + CH_2jSCH_2CHO$,

$CH_3SCH_2CHO \rightarrow H\bullet + CH_3SCHjCHO$ and

$CH_3SCH_2CHO \rightarrow H\bullet + CH_3SCH_2CjO$, respectively.

Similarly, the bond energies of H--CH_2CH_2SCHO, CH_3CH(--H)SCHO, and CH_3CH_2SC(=O)--H in CH_3CH_2SCHO, and the bond energies of H—$CH_2SC(=O)CH_3$ and $CH_3SC(=O)C(\text{--}H)H_2$ in $CH_3SC(=O)CH_3$ are calculated using the respective reactions shown in Table 2.3, in which the enthalpy of the parents and radicals are from the Hf data from Table 2.2.

Table 2.3 C—H Bond Energies (kcal/mol).

Parent		Radical			**Bond Energy**
CH_3SCH_2CHO	=	$C{\bullet}H_2SCH_2CHO$	+	H•	**CH_2(--H)SCH_2CHO**
-34.9		8.4		52.1	8.4+52.1-(-34.9) = 95.4
CH_3SCH_2CHO	=	$CH_3SC{\bullet}HCHO$	+	H•	**CH_3SCH(--H)CHO**
-34.9		-3.3		52.1	-3.3+52.1-(-34.9) = 83.7
CH_3SCH_2CHO	=	$CH_3SCH_2C{\bullet}{=}O$	+	H•	**CH_3SCH_2C(--H)$=O$**
-34.9		4.8		52.1	4.8+52.1-(-34.9) = 91.8
CH_3CH_2SCHO	=	$C{\bullet}H_2CH_2SCHO$	+	H•	**CH_2(--H)CH_2SCHO**
-43.0		5.4		52.1	5.4+52.1-(-43.0) = 100.5
CH_3CH_2SCHO	=	$CH_3C{\bullet}HSCHO$	+	H•	**CH_3CH(--H)$SCHO$**
-43.0		0.9		52.1	0.9+52.1-(-43.1) = 96.0
CH_3CH_2SCHO	=	$CH_3CH_2SC{\bullet}{=}O$	+	H•	**CH_3CH_2SC(--H)$=O$**
-43.0		-5.1		52.1	-5.1+52.1-(-43.1) = 90.0
$CH_3SC(=O)CH_3$	=	$C{\bullet}H_2SC{=}OCH_3$	+	H•	**CH_2(--H)$SC(=O)CH_3$**
-50.1		-5.7		52.1	-5.7+52.1-(-50.1) = 96.5
$CH_3SC(=O)CH_3$	=	$CH_3SC{=}OC{\bullet}H_2$	+	H•	**$CH_3SC(=O)CH_2$(--H)**
-50.1		-3.5		52.1	-3.5+52.1-(-50.1) = 98.7

Bond Energies :	H—CH_2SCH_2CHO	CH_3SCH(—H)CHO	CH_3SCH_2C(—H)$=O$	
	95.4,	83.7	91.8	kcal/mol.

Bond Energies:	H—CH_2CH_2SCHO	CH_3CH(—H)$SCHO$	CH_3CH_2SC(—H)O	
	100.5	96.0	90.0	kcal/mol.

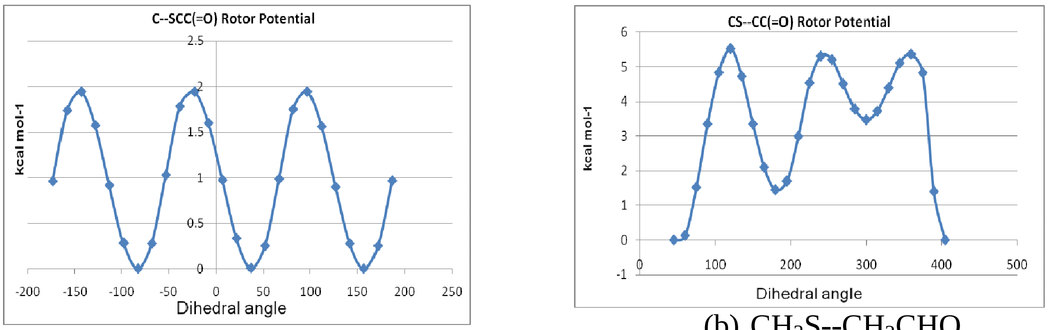
Bond Energies :	H—$CH_2SC(=O)CH_3$	$CH_3SC(=O)$ CH_2—H
	96.5	98.7 kcal/mol.

2.2.4 Frequencies and Moment of Inertia

The frequencies and the moments of inertia of the parent molecules and the corresponding radicals are listed in Table A.1 in Appendix A. These parameters are needed for SMCPS calculation of the thermo chemical properties at different temperatures, and they're used as frequencies and rotational spectroscopic constants as in FTIR and microwave analysis. They're from the highest CQS-QB3 output files of the corresponding species.

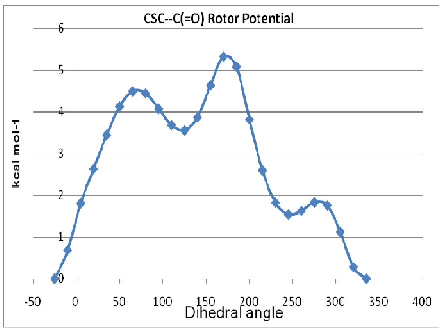
2.2.5 Internal Rotational Potentials

Internal rotor potentials analysis are of value to chemists working in molecular mechanics and in force field determinations in order to calibrate their force field models for energy versus dihedral angle, and it's a useful method of determining the lowest energy structure. As noted above they are also required to determine the lowest energy configuration of each molecule. The internal rotation potentials also indicate the relative energies and barriers to conversion between the conformers. They are also to be used to determine the entropy and heat capacity contributors from the internal rotors in the following work. The energy as a function of rotation about the dihedral angle was computed by scanning the angle from 0° to 360^{o} in steps of 15^{o}, and the remaining coordinates were optimized at UB3LY/3-21G level of theory. Figure 2.4-2.14 illustrates the internal rotor potentials of the parent molecule and their corresponding radicals, as mentioned in section 2.2.6.



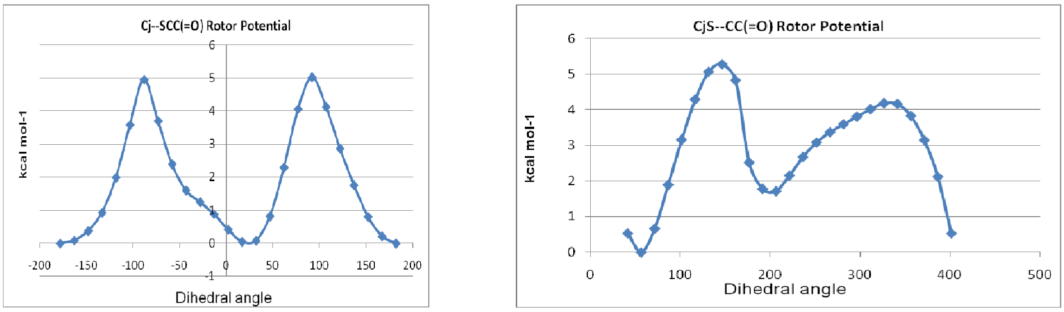
(a) CH3--SCH2CHO

(b) CH_3S--CH_2CHO



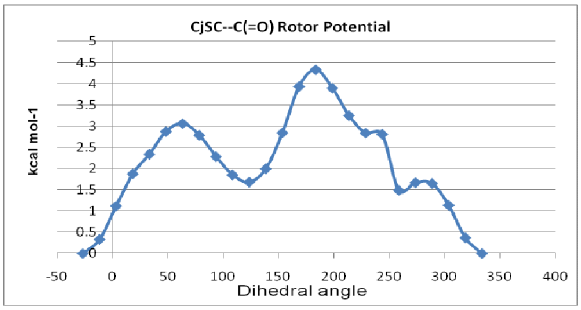
(c) CH_3SCH_2—CHO

Figure 2.4 Potential energy barriers for internal rotations in CH_3SCH_2CHO at UB3LY/3-21G level.



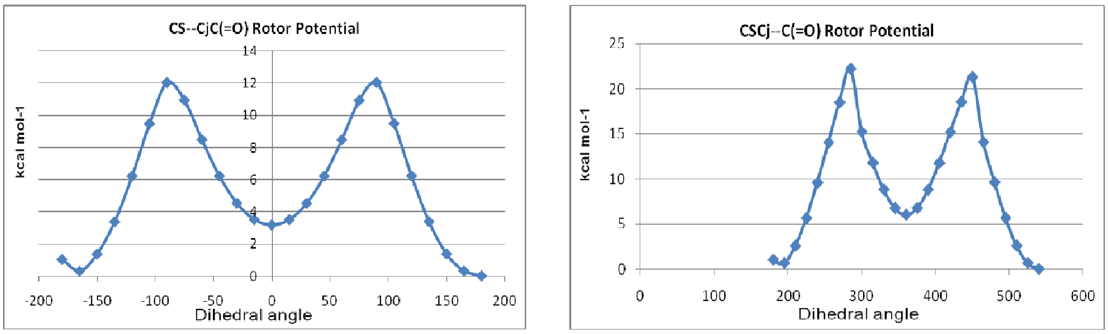
(a) CH_2j--SCH_2CHO

(b) CH_2jS--CH_2CHO



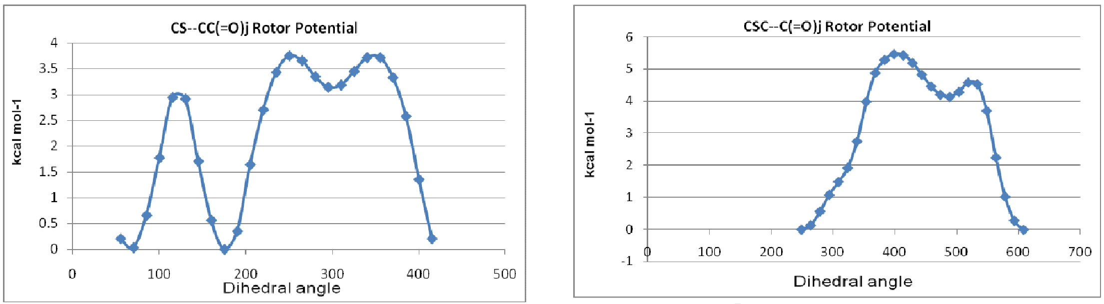
(c) CH_2jSCH_2--CHO

Figure 2.5 Potential energy barriers for internal rotations in CH_2jSCH_2CHO at UB3LY/3-21G level.



(a) CH_3S--CHjCHO (b) CH_3SCHj--CHO

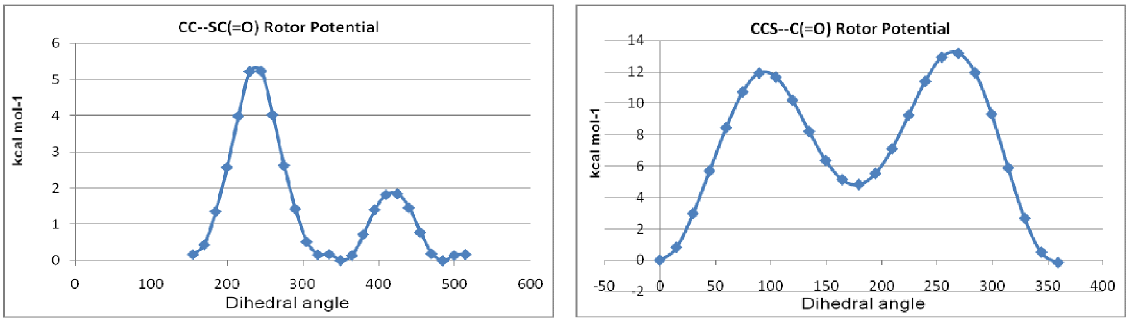
Figure 2.6 Potential energy barriers for internal rotations in CH_3SCHjCHO at UB3LY/3-21G level.



(a) CH_3S--CH_2Cj=O **(b)** CH_3SCH_2—Cj=O

Figure 2.7 Potential energy barriers for internal rotations in CH_3SCH_2Cj=O at UB3LY/3-21G level.

CH_3SCH_2CHO has the internal rotors of C—SCC(=O), CS—CC(=O) and CSC—C(=O), as demonstrated in Figure 2.4 (a), (b) and (c) respectively, their barriers are respectively 2, 5.5 and 5.4 kcal/mol. The first radical, CH_2jSCH_2CHO, has the rotators of Cj—SCC(=O), CjS—CC(=O) and CjSC—C(=O), and their barriers are 5, 5.3 and 4.4, respectively, as shown in Figure 2.5 (a), (b) and (c). The second radical, CH_3SCHjCHO, the barriers of its following rotators: CS—CjC(=O) and CSCj—C(=O) are 12 and 22 kcal/mol, as in Figure 2.6 (a) and (b). Then the third radical, CH_3SCH_2CjO, the barriers of its rotators of CS—CC(=O)j and CSC—C(=O)j are 3.7 and 5.4 kcal/mol, it's shown in Figure 2.7 (a) and (b).



(a) CH_3CH_2--SCHO (b) CH_3CH_2S--CHO

Figure 2.8 Potential energy barriers for internal rotations in CH_3CH_2SCHO at UB3LY/3-21G level.

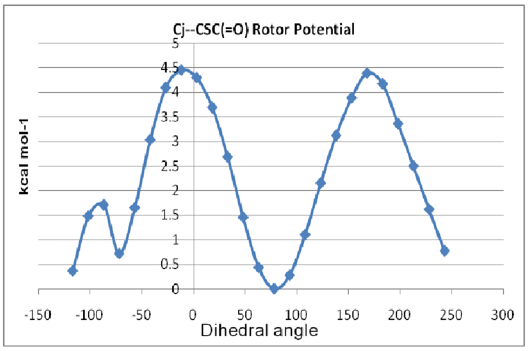
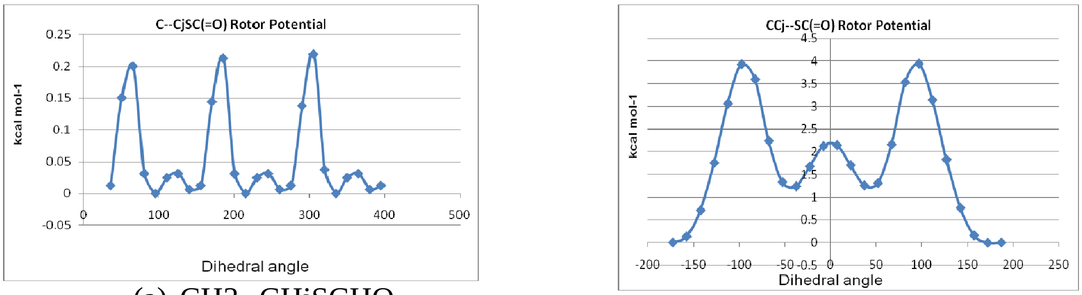
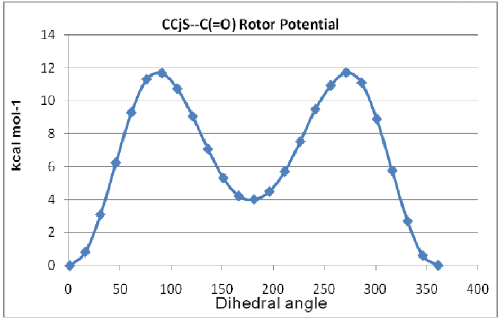


Figure 2.9 Potential energy barriers for internal rotations in CH_2jCH_2SCHO at UB3LY/3-21G level.



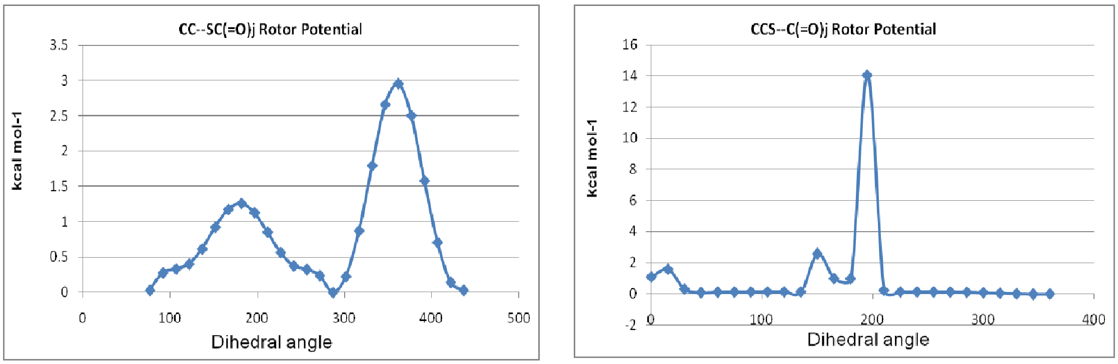
(a) CH3--CHjSCHO

(b) CH_3CHj--SCHO



(c) CH_3CHjS—CHO

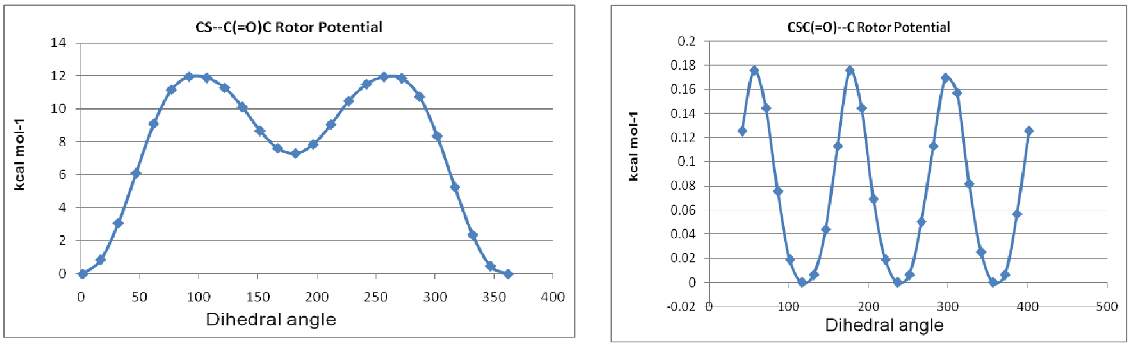
Figure 2.10 Potential energy barriers for internal rotations in $CH_3CHjSCHO$ at UB3LY/3-21G level.



(a) CH3CH2--SCj=O (b) CH_3CH_2S--Cj=O

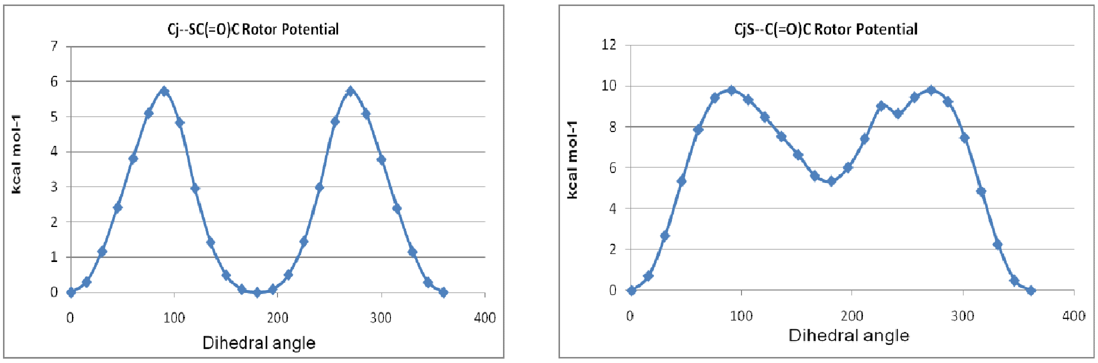
Figure 2.11 Potential energy barriers for internal rotations in $CH_3CH_2SCj{=}O$ at UB3LY/3-21G level.

For the parent molecule of CH_3CH_2SCHO in Figure 2.8, its rotor of CC—SC(=O) and CCS—C(=O) are 5.3 and 13.3 kcal/mol, as seen respectively in Figure 2.8 (a) and (b). The first radical in Figure 2.9, CH_2jCH_2SCHO, its rotor of Cj—CSC(=O) is 4.5kcal/mol. The second radical, $CH_3CHjSCHO$, its rotors are C—CjSC(=O), CCj—SC(=O) and CCjS—C(=O), their barriers are respectively 0.22, 4 and 11.8kcal/mol, as demonstrated in Figure 2.10 (a), (b) and (c). The third radical, CH_3CH_2SCjO, the barriers of its rotors of CC—SC(=O)j and CCS—C(=O)j are 3 and 14kcal/mol, as in Figure 2.11 (a) and (b).



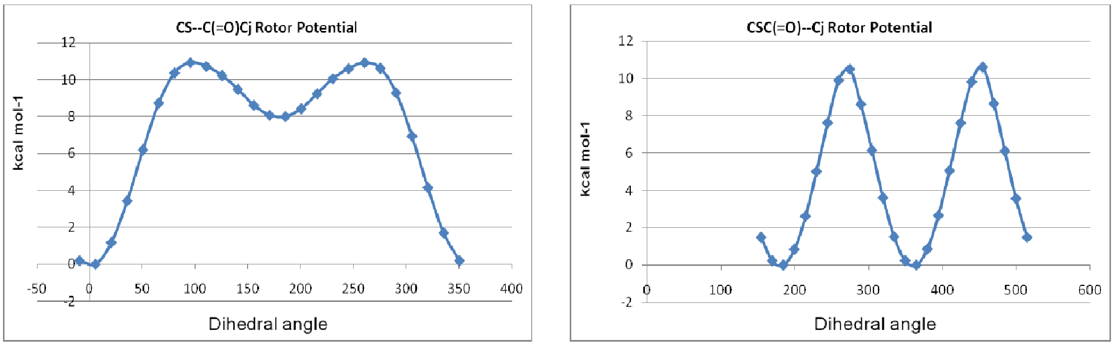
(a) CH_3S--C(=O)CH_3 (b) CH_3SC(=O)--CH_3

Figure 2.12 Potential energy barriers for internal rotations in $CH_3SC(=O)CH_3$ at UB3LY/3-21G level.



(a) CH_2j--SC(=O)CH_3 (b) CH_2jS--C(=O)CH_3

Figure 2.13 Potential energy barriers for internal rotations in $CH_2jSC(=O)CH_3$ at UB3LY/3-21G level.



(a) CH_3S--C(=O)CH_2j **(b)** $CH_3SC(=O)$--CH_2j

Figure 2.14 Potential energy barriers for internal rotations in $CH_3SC(=O)CH_2j$ at UB3LY/3-21G level.

Then, for $CH_3SC(=O)CH_3$, its rotors of CS—C(=O)C and CSC(=O)—C are 12 and 0.18kcal/mol as in Figure 2.12 (a) and (b). Its first radical, $CH_2jSC(=O)CH_3$, the rotors of Cj—SC(=O)C and CjS—C(=O)C, their barriers are 5.8 and 9.9kcal/mol, as in Figure 2.13 (a) and (b). Then its second radical, $CH_3SC(=O)CH_2j$, its rotors of CS—C(=O)Cj and CSC(=O)—Cj, the barriers are 10.8 and 10.6kcal/mol, as in Figure 2.14 (a) and (b).

2.2.6 S°298 and Cp°(T)

Entropy and heat capacity values from vibration, translation and rotation contributions are calculated using SMCPS and the Rotor programs. The scaled vibrations and the moment of inertia are from the optimized geometries under CBS-QB3, (scaled by the factor of 0.9613). Table 2.4 lists the data about 298K entropy and heat capacity vs. temperature of parent CH_3SCH_2CHO, CH_3CH_2SCHO and $CH_3SC(=O)CH_3$ accompanied by those of their radicals after one H atom departure, and the ideal gas-phase thermodynamic property vs. temperature data of each species are listed in Table B.1-B.3 in Appendix B, with a temperature range of 1-5000K. All these data are ideal gas thermodynamic properties at standard state (P=1atm and T=298K). To note, torsion frequencies are used for internal rotor contribution, with the ROTOR in the SMCPS input files being 0.

Table 2.4 298K Entropy and Data of Heat Capacity vs. Temperature

Species	**S°_{298K}**	**Cp300**	**Cp400**	**Cp500**	**Cp600**	**Cp800**	**Cp1000**	**Cp1500**
CH_3SCH_2CHO	80.3	23.2	28.1	32.4	36.1	41.9	46.1	52.6
CH_2jSCH_2CHO	79.6	24.0	28.3	32.0	35.0	39.6	43.0	48.2
$CH_3SCHjCHO$	78.6	22.3	26.9	30.8	34.0	39.0	42.6	48.0
$CH_3SCH_2Cj=O$	80.1	23.0	27.4	31.1	34.2	39.0	42.5	48.0
CH_3CH_2SCHO	79.0	22.8	27.8	32.1	35.8	41.7	45.9	52.5
CH_2jCH_2SCHO	77.9	23.6	28.1	31.8	34.8	39.5	42.9	48.2
$CH_3CHjSCHO$	81.3	23.4	27.6	31.3	34.4	39.2	42.7	48.2
CH_3CH_2SCjO	79.4	22.8	27.0	30.6	33.8	38.7	42.3	47.9
$CH_3SC(=O)CH_3$	81.1	24.0	28.7	32.8	36.4	42.0	46.1	52.5
$CH_2jSC(=O)CH_3$	80.1	24.6	28.8	32.3	35.2	39.7	43.0	48.2
$CH_3SC(=O)CH_2j$	78.9	23.8	28.2	31.9	34.9	39.5	42.9	48.1

2.3 Summary

Thermochemical parameters $\Delta_f H^o(298)$, standard entropy at 298.15 K and entropy and heat capacities form 1 to 5000K are presented for the lowest energy conformers of three proposed main products of atmospheric methyl ethyl partial oxidation: CH_3SCH_2CHO, CH_3CH_2SCHO and $CH_3SC(=O)CH_3$, and their radicals corresponding to loss of an H atom from the different C atom sites in the molecule. Bond energies, Internal Rotational Barrier plots, vibrational qualities and stable molecular structures have also been calculated and listed out. They were optimized using density functional theory and composite method CBS-QB3 methods in computational chemistry. Enthalpies from all the work reactions and at each of the calculation levels are in reasonably good agreement, however the CBS-QB3 results are the highest calculation level and these values are recommended for use. The use of the B3LYP density functional method with the 6-31G(d,p) and 6-31+G(2d,p) basis sets and work reactions with bond balance work well for these sulfur carbonyl species. The recommended Enthalpies of formation for CH_3SCH_2CHO, CH_3CH_2SCHO and $CH_3SC(=O)CH_3$ are -34.9, -43.0 and -50.1 kcal/mol respectively. C—H bond energies adjacent to sulfur atoms are weakened as a result of the electron resonance with the Sulfur. Internal Rotor potentials are also reported for use in molecular mechanics.

CHAPTER 3

STRUCTURES, THERMOCHEMISTRY, INTERNAL ROTOR POTENTIALS AND CARBON – HYDROGEN BOND ENERGIES IN METHYL ETHYL SULFIDE AND INTERMEDIATES OF RADICAL REACTIONS WITH O_2

Overview

The structure and thermochemical parameters ($\Delta_f H^o(298)$, S^o and Cp(T)), internal rotor potentials and carbon--hydrogen bond energies for ethyl methyl sulfide, and its radicals corresponding to loss of hydrogen atom were studied. The corresponding ethyl methyl sulfide alkyl hydroperoxides, peroxy radicals and hydroperoxide alkyl radicals were also studied in preparation for kinetic studies on the oxidation of ethyl methyl sulfide under atmospheric and combustion conditions. The thermochemical and structural properties were determined using computational chemistry.

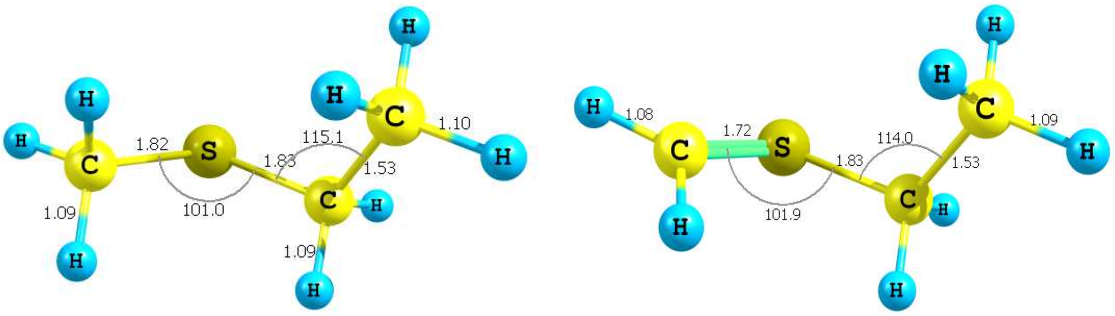
3.1 Calculation Methods

Calculations are based on Density Functional Theory (DFT) and composite ab initio levels using Gaussian 98 and Gaussian 03. Computation levels include B3LYP/6-31G(d,p), and B3LYP/6-31+G(2d,p), and the higher level composite CBS-QB3 method. CBS-QB3 [1] is a complete basis set method that uses geometries and frequencies from the B3LYP/6-311G(2d,d,p) level followed by single point energy calculations at the MP2, MP4SDQ, and CCSD(T) levels. The final energies are determined with a CBS extrapolation. All calculations were performed using the Gaussian 03 program suite. Enthalpies of formation for stable species are calculated using the calculated total energies (298K) from each of the calculation levels with work reactions that are isodesmic in most cases. Isodesmic reactions conserve the number and type of bonds on both sides of an equation. The use of a work reaction with similar bonding on both sides of an equation results in a cancellation of calculation error and improves the accuracy for energy analysis. The reported enthalpy values can be compared with the known enthalpies of several molecules in the system to serve as a calibration on the thermochemistry and the Potential Energy (PE) diagram for reaction of the ethyl methyl sulfide radicals with molecular oxygen. The entropy and heat capacity (S°(T) and Cp°(T)) are calculated using the "SMCPS" (Statistical Mechanics for Heat Capacity and Entropy Cp and S) program which incorporates data on the frequencies, moments of inertia, molecular mass, symmetry and number of optical isomers from the B3LYP/6-31G(2d,2p) calculation in the CBS-QB3 method. Torsion frequencies are used for internal rotor contribution.

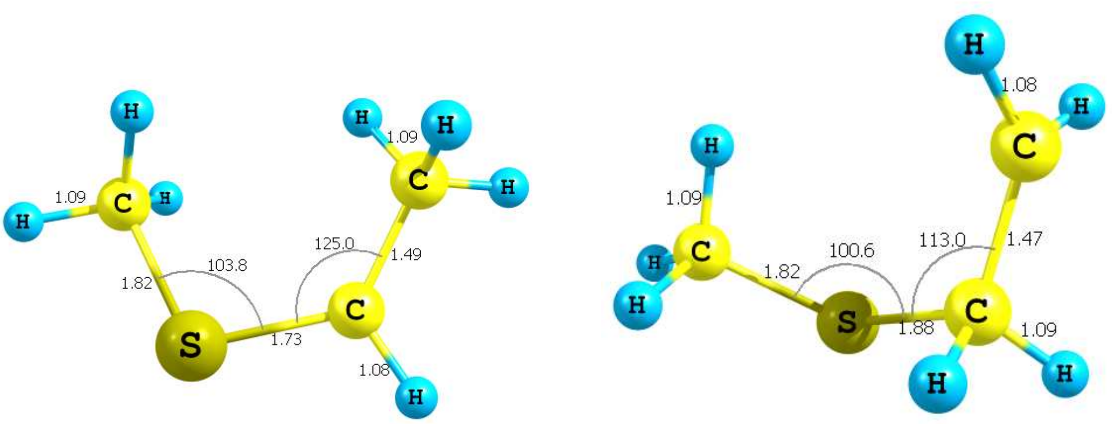
3.2 Results and Discussion

3.2.1 Structure

The lowest energy structure for each molecule and radical has been confirmed by comparing the lowest energy dihedral from the internal rotation potential curve with the structural parameter obtained from CBS-QB3 output file, the highest applied calculation level with the highest precision. Their detailed structural information for all the species to study are shown in Figure 3.1-3.8, in which the dihedrals to study in the stable molecules and radicals are noted below each species image.



(a) $CH_3SCH_2CH_3$ C-S-C-C =-70.7˚ (b) $CH_2jSCH_2CH_3$ C-S-C-C =-70.6˚



(c) $CH_3SCHjCH_3$ C-S-C-C =36.3˚ **(d)** $CH_3SCH_2CH_2j$ C-S-C-C =-67.5˚

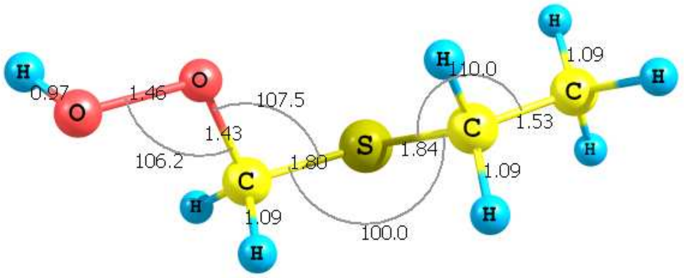
Figure 3.1 Optimized structures of $CH_3SCH_2CH_3$, $CH_2jSCH_2CH_3$, $CH_3SCHjCH_3$ and $CH_3SCH_2CH_2j$ at CBS-QB3 level (Bond distances in Å; Bond Angles in ^{o}).

In $CH_3SCH_2CH_3$, as shown in Figure 3.1 (a), all the H—C bonds are also 1.1±0.02A°, both the C—SCC bond and CS—CC bond are 1.82 and 1.83A°, CSC—C is 1.53A°. The C—S—CC angle is 101.0^o, the CS—C—C angle is 115.1^o.

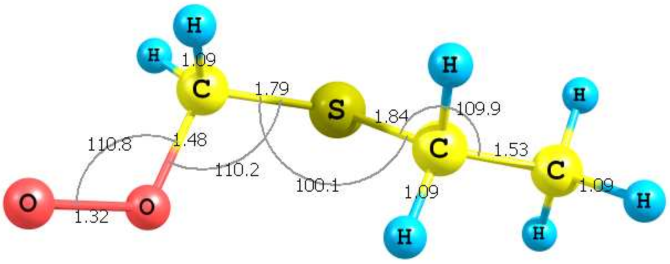
Then, for the radicals: 1) in $CH_2jSCH_2CH_3$, as shown in Figure 3.1 (b), there is no evident change in the lengths of all the C—H bonds and each internal bond angle, but the bond of C—SCC has shortened to 1.72A°; 2)in $CH_3SCHjCH_3$, as shown in Figure 3.1 (c), the angle of C—S—CC has increased to 103.8°, CS—C—C has evidently increased to 125.0°, and CS—CC has shortened to 1.73A°, but there is also no evident change in each C--H bond; 3) in $CH_3SCH_2CH_2j$, as shown in Figure 3.1 (d), CS—C—C has undergone minor decrease to 113.0° and CS—CC has increased to 1.88A°.

Similar to the structures in Chapter 2, after one H atom is abstracted from carbon atom there is an unpaired electron on it, and this unpaired electron can interact with neighboring atoms. A bond shortening is observed and suggests that the electronic interaction is enhanced between the C—S bonds and C—H bonds. Removal of an H atom on the methyl side of a sulfur atom will lead to formation a partial double bond: $C\underline{\bullet}SCC$, which is participated by another pair of unpaired electrons on both sulfur and carbon atoms.

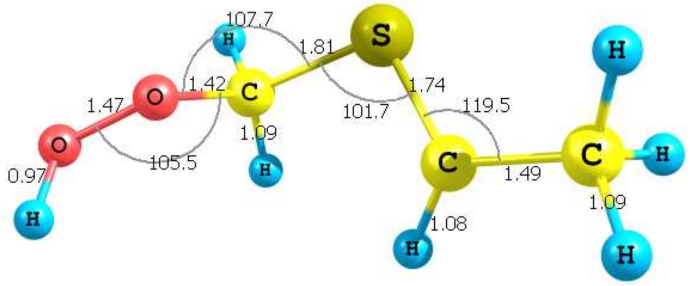
The partial oxidation intermediates ethyl-methylsulfide radicals are peroxy radicals. To study the peroxy radicals, this section starts with the stable hydroperoxides on the different carbon sites of the $CH_3SCH_2CH_3$: $HOOCH_2SCH_2CH_3$, $CH_3SCH(OOH)CH_3$ and $CH_3SCH_2CH_2OOH$. The structures of these hydroperoxides are demonstrated in Figure 3.2, 3.3 and 3.4 respectively. In their radicals formed after one H atom removed from stable molecules, compared to their stable molecules, there is also no evident change on each C—H bond length, and the other changes are similar to the formation of radicals from $CH_3SCH_2CH_3$. The bond between two O atoms decreases significantly from about 1.5A° to near 1.3A° after the H atom departure from the –OOH group. This is brought about by the interaction between the unpaired electron on the outer oxygen atom with the electrons on the inner oxygen atom next to the carbon: this effectively results in an RO=O• double bond.



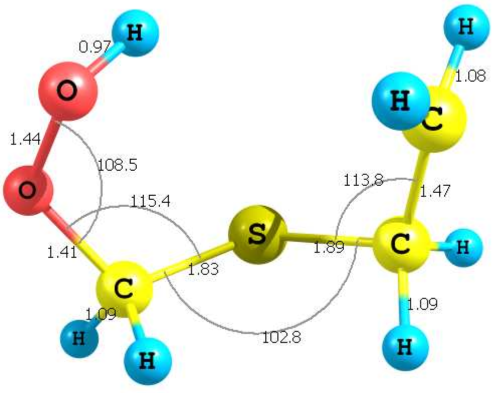
(a) $HOOCH_2SCH_2CH_3$ O-O-C-S =-173.5° O-C-S-C =72.6° C-S-C-C =-176.4°



(b) $jOOCH_2SCH_2CH_3$ O-O-C-S =162.2° O-C-S-C =-73.0° C-S-C-C =178.7°

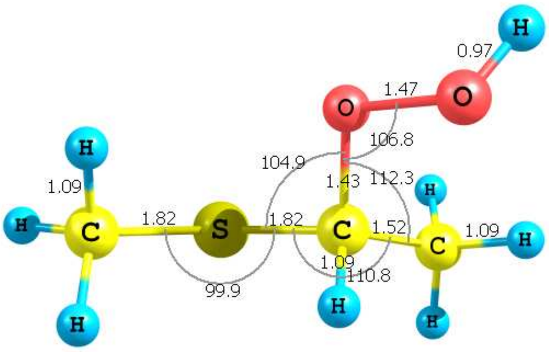


(c) $HOOCH_2SCHjCH_3$ O-O-C-S =-178.8° O-C-S-C =77.1° C-S-C-C =-172.1°

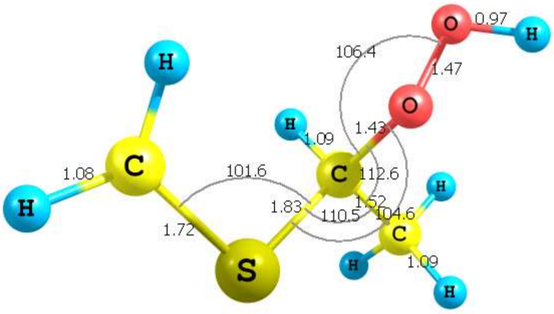


(d) $HOOCH_2SCH_2CH_2j$ O-O-C-S =-72.4° O-C-S-C =104.7° C-S-C-C =-79.8°

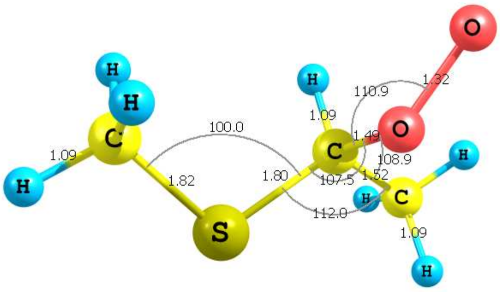
Figure 3.2 Optimized structures of $HOOCH_2SCH_2CH_3$, $jOOCH_2SCH_2CH_3$, $HOOCH_2SCHjCH_3$ and $HOOCH_2SCH_2CH_2j$ at CBS-QB3 level (Bond distances in Å; Bond Angles in °).



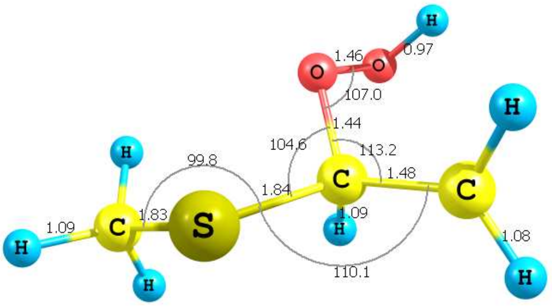
(a) $CH_3SCH(OOH)CH_3$ C-S-C-C =170.7˚ C-S-C-O =-67.9˚ S-C-O-O =165.6˚



(b) $CH_2jSCH(OOH)CH_3$ C-S-C-C =-171.5˚ C-S-C-O =67.0˚ S-C-O-O =-166.1˚

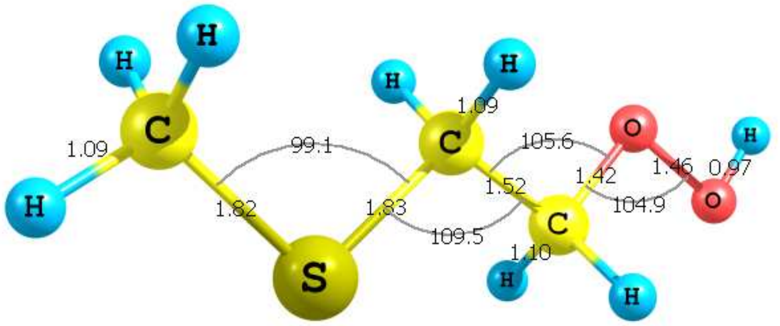


(c) $CH_3SCH(OOj)CH_3$ C-S-C-C =-172.2˚ C-S-C-O =68.2˚ S-C-O-O =-158.2˚

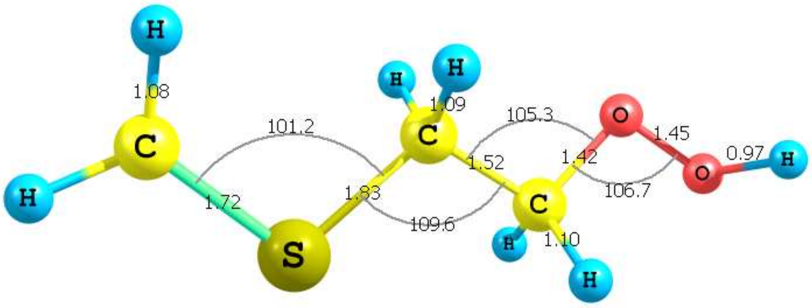


(d) $CH_3SCH(OOH)CH_2j$ C-S-C-C =-168.4˚ C-S-C-O =69.7˚ S-C-O-O =-164.5˚

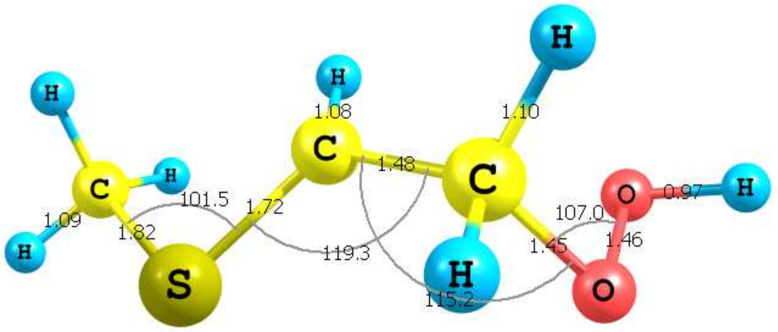
Figure 3.3 Optimized structures of $CH_3SCH(OOH)CH_3$, $CH_2jSCH(OOH)CH_3$, $CH_3SCH(OOj)CH_3$ and $CH_3SCH(OOH)CH_2j$ at CBS-QB3 level (Bond distances in Å; Bond Angles in º).



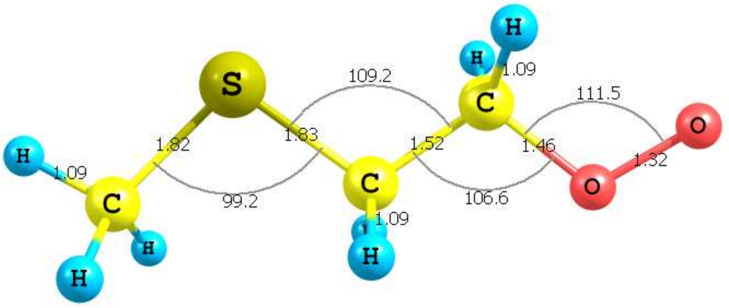
(a) $CH_3SCH_2CH_2OOH$ C-S-C-C =180˚ S-C-C-O =180˚ C-C-O-O =-180˚



(b) $CH_2jSCH_2CH_2OOH$ C-S-C-C =178.6˚ S-C-C-O =-178.6˚ C-C-O-O =-175.8˚



(c) $CH_3SCHjCH_2OOH$ C-S-C-C =178.5˚ S-C-C-O =81.7˚ C-C-O-O =67.1˚



(d) $CH_3SCH_2CH_2OOj$ C-S-C-C =-180.0˚ S-C-C-O =-180.0˚ C-C-O-O =-180.0˚

Figure 3.4 Optimized structures of $CH_3SCH_2CH_2OOH$, $CH_2jSCH_2CH_2OOH$, $CH_3SCHjCH_2OOH$ and $CH_3SCH_2CH_2OOj$ at CBS-QB3 level (Bond distances in Å; Bond Angles in º).

In addition to the peroxy radicals, the alcohols and the alkoxy radicals were also calculated. The peroxy radicals are formed in combustion and in atmospheric chemistry by reaction of the ethyl-methyl sulfide radicals with O2. Then, in the atmosphere, the peroxy radicals react with nitric oxide (NO) to form NO2 and alkoxy radicals.

$CH_3SCH_2CH•_2 + O2 = CH_3SCH_2CH_2OO•$ and

$CH_3SCH_2CH_2OO• + NO = CH_3SCH_2CH_2O• + NO2$ $\Delta HRxn = - 13\ kcal\ mol^{-1}$

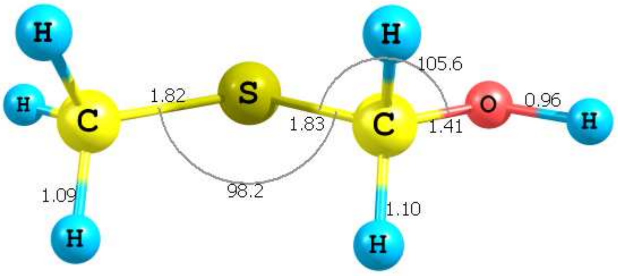
Sulfoxides are formed in atmospheric and combustion chemistry via reactions with OH radical and O_2.

$CH_3SCH_2CH_3 + OH = CH_3S•(\text{-}OH)CH_2CH_3$ and

$CH_3S•(\text{-}OH)CH_2CH_3 + O_2 = [CH_3S•(OO•(\text{-}OH)CH_2CH_3\ ] = CH_3S(=O)CH_2CH_3 + HO_2$

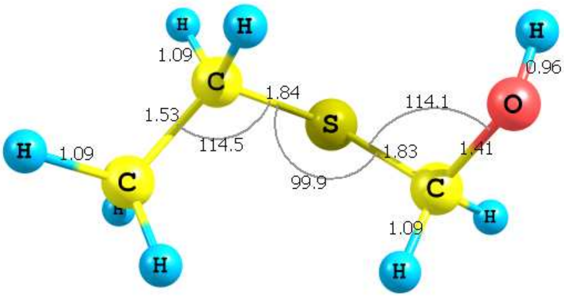
The $[CH_3S•(\text{-}OH)CH_2CH_3]$ and $[CH_3S•(OO•(\text{-}OH)CH_2CH_3\ ]$ are both loosely bound adducts and exist is a quasi equilibria under atmospheric conditions. Under combustion conditions the adducts dissociate back to reactants very quickly.

The optimized structures for several of these intermediates CH_3SCH_2OH, $CH_3CH_2SCH_2OH$, $CH_3S(=O)CH_2OH$ and $CH_3S(=O)CH(OH)CH_3$ are determined, and reported in Figure 3.5-3.8.



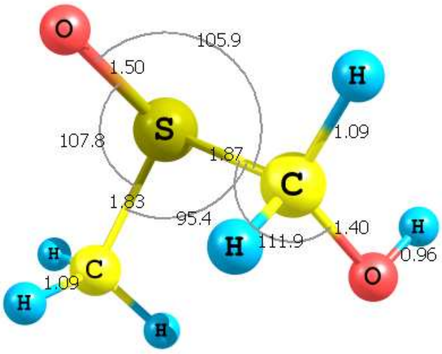
C-S-C-O =180 °

Figure 3.5 Optimized structure of CH_3SCH_2OH at CBS-QB3 level (Bond distances in Å; Bond Angles in °).



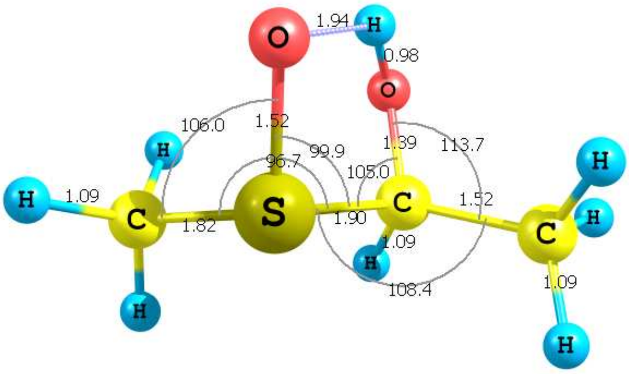
C-C-S-C =-79.9 º, C-S-C-O =-62.3 º

Figure 3.6 Optimized structure of $CH_3CH_2SCH_2OH$ at CBS-QB3 level (Bond distances in Å; Bond Angles in º).



O-C-S=O =176.5 º, O-C-S-C =66.2 º

Figure 3.7 Optimized structure of $CH_3S(=O)CH_2OH$ at CBS-QB3 level (Bond distances in Å; Bond Angles in º).



C-C-S-C =-164.2 º, C-C-S=O =88.2 º, C-S-C-O =74.0 º

Figure 3.8 Optimized structure of $CH_3S(=O)CH(OH)CH_3$ at CBS-QB3 level (Bond distances in Å; Bond Angles in º).

In Figure 3.8, it can be seen that at the lowest energy point of $CH_3S(=O)CH(OH)CH_3$, a hydrogen bond has been formed between the O atom on the sulfur and the H atom on the hydroxyl group.

3.2.2 Heats of Formation and Enthalpies of Reaction

Similar to the calculations in Chapter 2, enthalpies of formation $\Delta_f H^o(298)$ of the target parent and radical intermediates have been determined using calculated $\Delta_f H^o(298)$ values for each species, then calculating the ΔHreaction at 298 K, and then using the known literature values for the three reference molecules in the work reaction and the calculated ΔHrxn find $\Delta_f H^o(298)$ of the target. The standard enthalpies of formation of the reference species at 298K used in the work reactions are summarized in Table 3.1. For radical species, the work reactions included the parent molecule and applied the enthalpy value of the parent determined in this study as a reference.

$$\Delta H\text{rxn} = \Sigma\ \Delta_f H^o\ (298)\ \text{products}\ - \Sigma\ \Delta_f H^o\ (298)\ \text{reactants}$$

The work reactions in Table 3.2 are used to calculate the heat of reaction and enthalpies of formation for the stable molecules of $CH_3SCH_2CH_2$, $HOOCH_2SCH_2CH_3$, $CH_3SCH(OOH)CH_3$ and $CH_3SCH_2CH_2OOH$, and their radicals after removal of one H atom from the carbon atom and peroxy oxygen sites. The work reactions for the following molecules are also included in Table 3.2: CH_3SCH_2OH, $CH_3CH_2SCH_2OH$, $CH_3S(=O)CH_2OH$ and $CH_3S(=O)CH(OH)CH_3$. Also, all the enthalpy calculations and the reported values are based on the lowest energy conformer.

Energies are calculated at the composite CBS-QB3, B3LYP/6-31+g(2d,p) and B3LYP/6-31g(d,p) levels. CBS-QB3 is the highest level among all applied calculations. Average values over the three calculation methods for each work reaction, and separately the average values over the work reactions for each calculation method are presented. The average value over the work reactions at the CBS-QB3 level are recommended

$\Delta_f H^o(298)$, as this method has the highest accuracy. $\Delta_f H^o(298)$ data are reported for each species.

The resultant CBS-QB3 Hf values from the work reactions in Table 3.2 are recommended when studying the C—H bond energies in section 3.2.3. These are also the values used in reporting the thermochemical properties in the tables below.

Information in the CBS-QB3 output file are used for the inertias and frequencies to input in the SMCPS input files, and to get the most stable structures of the species.

On a relative scale for sites on the same molecule, the higher the enthalpy, the less stable the radical and usually the more difficult to form.

Table 3.1 Standard Enthalpies of Formation of Reference Species at 298.15 K.

Species	$\Delta H_{f}{}^{o}{}_{298}$(kcal mol^{-1})	Reference
CH_3CH_3	-20.04	[14]
CH_3SCH_3	-8.96	[8]
$CH_3CH_2CH_3$	-24.82	[14]
$CH_3CH_2SCH_2CH_3$	-20	[12]
CH_2jCH_3	29.1	[18]
$CH_2jCH_2CH_3$	23.67	[8]
CH_3CHjCH_3	21.02	[8]
$CH_3S(=O)CH_3$	-35.97	[16]
$CH_3CH_2S(=O)CH_3$	-41.77	[16]
CH_3CH_2SH	-11.03	[12]
$CH_3CH(OOH)CH_3$	-49.93	[17]
$CH_3CH(OOH)SH$	-36.29	[11]
CH_3CH_2OOH	-40.1	[17]
$CH_3CH(OOj)CH_3$	-15.2	[17]
CH_3CH_2OOj	-6.72	[5]
CH_2jCH_2OOH	10.9	[5]
$CH_2jCH(OOH)CH_3$	1.6	[5]
CH_2jSCH_3	32.66	[11]
$CH_3CH_2CH_2OOH$	-46.56	[11]
$CH_3CH_2CH_2OOj$	-12.62	[11]
CH_3CH_2OH	-56.23	[8]
$CH_3CH_2CH_2OH$	-61.13	[8]
CH_3SCH_2OH	-41.6	This work
CH3CH2SCH2OH	-52.8	This work

Table 3.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation (ΔH^o_{f298}) of the Parents and the Radicals[a] (Units: kcal/mol) [a].

Work Reactions	**$\Delta H_f{}^o{}_{298}$(kcal mol^{-1})**		**CBS-QB3**	**Average**
	b3lyp/6-31G(d,p)	**b3lyp/6-31+G(2d,p)**		
$CH_3SCH_2CH_3$				
$CH_3SCH_2CH_3 + CH_3CH_2CH_3 \rightarrow CH_3CH_2SCH_2CH_3 + CH_3CH_3$	-15.0	-15.0	-14.7	-14.9
$CH_3SCH_2CH_3 + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_3CH_2CH_3$	-14.0	-14.0	-14.4	-14.1
$CH_3SCH_2CH_3 + CH_3SCH_2CH_3 \rightarrow CH_3SCH_3 + CH_3CH_2SCH_2CH_3$	-14.5	-14.5	-14.5	-14.5
Average of all the work reactions	-14.5	-14.5	**-14.5**	-14.5
Hf=-14.5, the average of the CBS-QB3 level				
$CH_2jSCH_2CH_3$				
$CH_2jSCH_2CH_3 + CH_3CH_2CH_3 \rightarrow CH_3CH_2SCH_2CH_3 + CH_2jCH_3$	27.1	26.4	26.8	26.8
$CH_2jSCH_2CH_3 + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_2jCH_2CH_3$	27.3	26.6	25.7	26.5
$CH_2jSCH_2CH_3 + CH_3CH_2CH_3 \rightarrow CH_3CHjCH_3 + CH_3SCH_2CH_3$	28.3	27.3	26.5	27.4
$CH_2jSCH_2CH_3 + CH_3CH_2CH_3 \rightarrow CH_2jCH_2CH_3 + CH_3SCH_2CH_3$	26.7	26.1	25.6	26.2
Average	27.3	26.6	**26.2**	26.7
Hf=26.2, the average of the CBS-QB3 level				
$CH_3SCHjCH_3$				
$CH_3SCHjCH_3 + CH_3CH_2CH_3 \rightarrow CH_3CH_2SCH_2CH_3 + CH_2jCH_3$	25.5	25.3	26.5	25.8
$CH_3SCHjCH_3 + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_2jCH_2CH_3$	25.7	25.5	25.5	25.5
$CH_3SCHjCH_3 + CH_3CH_2CH_3 \rightarrow CH_3CHjCH_3 + CH_3SCH_2CH_3$	26.7	26.2	26.2	26.4
$CH_3SCHjCH_3 + CH_3CH_2CH_3 \rightarrow CH_2jCH_2CH_3 + CH_3SCH_2CH_3$	25.2	24.9	25.4	25.2
Average	25.8	25.5	**25.9**	25.7
Hf=25.9, the average of the CBS-QB3 level				
$CH_3SCH_2CH_2j$				
$CH_3SCH_2CH_2j + CH_3CH_2CH_3 \rightarrow CH_3CH_2SCH_2CH_3 + CH_2jCH_3$	32.5	32.6	33.9	33.0
$CH_3SCH_2CH_2j + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_2jCH_2CH_3$	32.7	32.8	32.8	32.8
$CH_3SCH_2CH_2j + CH_3CH_2CH_3 \rightarrow CH_3CHjCH_3 + CH_3SCH_2CH_3$	33.8	33.5	33.5	33.6
$CH_3SCH_2CH_2j + CH_3CH_2CH_3 \rightarrow CH_2jCH_2CH_3 + CH_3SCH_2CH_3$	32.2	32.3	32.7	32.4
Average	32.8	32.8	**33.2**	33.0
Hf=33.2, the average of the CBS-QB3 level				
$HOOCH_2SCH_2CH_3$				
$HOOCH_2SCH_2CH_3 + CH_3CH_2SH \rightarrow CH_3SCH_2CH_3 + CH_3CH(OOH)SH$	-37.1	-37.9	-36.4	-37.1
$HOOCH_2SCH_2CH_3 + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_3CH(OOH)CH_3$	-35.4	-36.1	-35.3	-35.6
Average	-36.2	-37.0	**-35.8**	-36.4
Hf=-35.8, the average of the CBS-QB3 level				
$jOOCH_2SCH_2CH_3$				
$jOOCH_2SCH_2CH_3 + CH_3CH_2OOH- \rightarrow HOOCH_2SCH_2CH_3 + CH_3CH_2OOj$	3.3	3.4	-2.0	1.6
$jOOCH_2SCH_2CH_3 + CH_3CH_2CH_2OOH \rightarrow HOOCH_2SCH_2CH_3 + CH_3CH_2CH_2OOj$	3.9	4.0	-1.7	2.1
Average	3.6	3.7	**-1.8**	1.8
Hf=-1.8, the average of the CBS-QB3 level				
$HOOCH_2SCHjCH_3$				
$HOOCH2SCHjCH3 + CH_3SCH_2CH_3 \rightarrow HOOCH_2SCH_2CH_3 + CH_3SCHjCH_3$	4.6	5.1	5.0	4.9
$HOOCH2SCHjCH3 + CH_3SCH_2CH_3 \rightarrow HOOCH_2SCH_2CH_3 + CH_3SCH_2CH_2j$	4.8	4.9	4.8	4.9
Average	4.7	5.0	**4.9**	4.9
Hf=4.9, the average of the CBS-QB3 level				
$HOOCH_2SCH_2CH_2j$				
$HOOCH_2SCH_2CH_2j + CH_3SCH_2CH_3 \rightarrow HOOCH_2SCH_2CH_3 + CH_3SCH_2CH_2j$	9.3	10.2	10.5	10.0
$HOOCH_2SCH_2CH_2j + CH_3SCH_2CH_3 \rightarrow HOOCH_2SCH_2CH_3 + CH_3SCHjCH_3$	9.1	10.3	10.6	10.0
Average	9.2	10.2	**10.5**	10.0
Hf=10.5, the average of the CBS-QB3 level				
$CH_3SCH(OOH)CH_3$				
$CH_3SCH(OOH)CH_3 + CH_3CH_2SH \rightarrow CH_3CH(OOH)SH + CH_3SCH_2CH_3$	-40.5	-40.4	-40.5	-40.5
$CH_3SCH(OOH)CH_3 + CH_3CH_3 \rightarrow CH_3CH(OOH)CH_3 + CH_3SCH_3$	-38.8	-38.6	-39.4	-38.9
Average	-39.7	-39.5	**-39.9**	-39.7
Hf=-39.9, the average of the CBS-QB3 level				
$CH_2jSCH(OOH)CH_3$				
$CH_2jSCH(OOH)CH_3 + CH_3SCH_2CH_3 \rightarrow CH2jSCH2CH3 +$	3.5	3.8	3.9	3.7
$CH_3SCH(OOH)CH_3$	3.0	3.6	3.7	3.4
$CH_2jSCH(OOH)CH_3 + CH_3SCH_3 \rightarrow CH2jSCH3 + CH_3SCH(OOH)CH_3$	3.2	3.7	**3.8**	3.6
Average				
Hf=3.8, the average of the CBS-QB3 level				
$CH_3SCH(OOj)CH_3$				
$CH_3SCH(OOj)CH_3+CH_3CH(OOH)CH_3 \rightarrow CH_3SCH(OOH)CH_3+CH_3CH(OOj)C$	-3.8	-4.0	-4.2	-4.0
H_3	-5.3	-5.5	-6.0	-5.6
$CH_3SCH(OOj)CH_3 + CH_3CH_2OOH-- \rightarrow CH_3SCH(OOH)CH_3 + CH_3CH_2OOj$	-4.6	-4.8	**-5.1**	-4.8
Average				
Hf=-5.1, the average of the CBS-QB3 level				

Table 3.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation ($\Delta H^o{}_{f298}$) of the Parents and the Radicals[a] (Units: kcal/mol) [a]. (Continued)

Work Reactions	**$\Delta H_f{}^o{}_{298}$(kcal mol^{-1})**		**CBS-QB3**	**Average**
	b3lyp/6-31G(d,p)	**b3lyp/6-31+G(2d,p)**		
$CH_3SCH(OOH)CH_2j$				
$CH_3SCH(OOH)CH_2j + CH_3CH_3 \rightarrow CH_2jCH_2OOH + CH_3SCH_2CH_3$	12.1	12.9	11.8	12.3
$CH_3SCH(OOH)CH_2j + CH_3CH_3 \rightarrow CH_2jCH(OOH)CH_3 + CH_3SCH_3$	11.8	12.0	11.6	11.8
Average	11.9	12.5	**11.7**	12.0
Hf=11.7, the average of the CBS-QB3 level				
$CH_3SCH_2CH_2OOH$				
$CH_3SCH_2CH_2OOH + CH_3CH_2SH \rightarrow CH_3CH(OOH)SH + CH_3SCH_2CH_3$	-35.0	-35.7	-34.7	-35.1
$CH_3SCH_2CH_2OOH + CH_3CH_3 \rightarrow CH_3CH(OOH)CH_3 + CH_3SCH_3$	-33.3	-33.9	-33.6	-33.6
Average	-34.2	-34.8	**-34.2**	-34.4
Hf=-34.2, the average of the CBS-QB3 level				
$CH_2jSCH_2CH_2OOH$				
$CH_2jSCH_2CH_2OOH + CH_3CH_3 \rightarrow CH_2jSCH_2CH_3 + CH_3CH_2OOH$	9.7	9.7	9.2	9.6
$CH_2jSCH_2CH_2OOH + CH_3CH_3 \rightarrow CH_2jSCH_3 + CH_3CH_2CH_2OOH$	7.8	8.0	7.5	7.8
Average	8.8	8.9	**8.3**	8.7
Hf=8.3, the average of the CBS-QB3 level				
$CH_3SCHjCH_2OOH$				
$CH_3SCHjCH_2OOH + CH_3SCH_2CH_3 \rightarrow CH_3SCH_2CH_2OOH +$	3.5	3.0	3.9	3.4
$CH_3SCH_2CH_2j$	3.3	3.1	4.0	3.4
$CH_3SCHjCH_2OOH + CH_3SCH_2CH_3 \rightarrow CH_3SCH_2CH_2OOH + CH_3SCHjCH_3$	3.0	3.0	**3.9**	3.4
Average				
Hf=3.9, the average of the CBS-QB3 level				
$CH_3SCH_2CH_2OOj$				
$CH_3SCH_2CH_2OOj+CH_3CH_2OOH \rightarrow CH_3SCH_2CH_2OOH + CH_3CH_2OOj$	-0.7	-0.8	-0.4	-0.7
$CH_3SCH_2CH_2OOj+CH_3CH_2CH_2OOH \rightarrow CH_3SCH_2CH_2OOH+CH_3CH_2CH_2O$	-0.2	-0.2	-0.1	-0.1
OH	-0.5	-0.5	**-0.3**	-0.4
Average				
Hf=-0.3, the average of the CBS-QB3 level				
CH_3SCH_2OH				
$CH_3SCH_2OH + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_3CH_2OH$	-40.8	-40.7	-41.8	-41.1
$CH_3SCH_2OH + CH_3CH_2CH_3 \rightarrow CH_3SCH_3 + CH_3CH_2CH_2OH$	-40.5	-40.6	-41.6	-40.9
Average	-40.6	-40.7	**-41.6**	-41.0
Hf=-41.6, the average of the CBS-QB3 level				
$CH_3CH_2SCH_2OH$				
$CH_3CH_2SCH_2OH + CH_3CH_3 \rightarrow CH_3SCH_3 + CH_3CH_2CH_2OH$	-53.4	-52.7	-53.0	-53.0
$CH_3CH_2SCH_2OH + CH_3CH_2CH_3 \rightarrow CH_3SCH_2CH_3 + CH_3CH_2CH_2OH$	-53.4	-52.7	-52.6	-52.9
Average	-53.4	-52.7	**-52.8**	-53.0
Hf=-52.8, the average of the CBS-QB3 level				
$CH_3S(=O)CH_2OH$				
$CH_3S(=O)CH_2OH + CH_3SCH_3 \rightarrow CH_3SCH_2OH + CH_3S(=O)CH_3$	-72.9	-71.3	-69.8	-71.4
$CH_3S(=O)CH_2OH + CH_3SCH_2CH_3 \rightarrow CH_3CH_2SCH_2OH + CH_3S(=O)CH_3$	-72.0	-71.2	-70.8	-71.3
$CH_3S(=O)CH_2OH + CH_3SCH_2CH_3 \rightarrow CH_3SCH_2OH + CH_3CH_2S(=O)CH_3$	-72.3	-71.1	-69.6	-71.0
Average	-72.4	-71.2	**-70.1**	-71.2
Hf=-70.1, the average of the CBS-QB3 level				
$CH_3S(=O)CH(OH)CH_3$				
$CH_3S(=O)CH(OH)CH_3+CH_3SCH_3 \rightarrow CH_3CH_2SCH_2OH + CH_3S(=O)CH_3$	-86.7	-83.7	-84.8	-85.1
$CH_3S(=O)CH(OH)CH_3+CH_3SCH_3 \rightarrow CH_3SCH_2OH + CH_3CH_2S(=O)CH_3$	-87.0	-83.6	-83.6	-84.7
$CH_3S(=O)CH(OH)CH_3+CH_3SCH_2CH_3 \rightarrow CH_3CH_2SCH_2OH+$	-86.1	-83.5	-84.5	-84.7
$CH_3CH_2S(=O)CH_3$	-86.6	-83.6	**-84.3**	-84.8
Average				
Hf=-84.3, the average of the CBS-QB3 level				

Table 3.3 C—H Bond Energies of $CH_3SCH_2CH_3$ Calculated in kcal/mol

					Bond Energy:
$CH_2{\bullet}SCH_2CH_3$	+	H•	=	$CH_3SCH_2CH_3$	CH_2(--H)SCH_2CH_3
26.2		52.1		-14.5	26.2+52.1-(-14.5) = 92.8
$CH_3SCH{\bullet}CH_3$	+	H•	=	$CH_3SCH_2CH_3$	CH_3SCH(--H)CH_3
25.9		52.1		-14.5	25.9+52.1-(-14.5) = 92.5
$CH_3SCH_2CH_2{\bullet}$	+	H•	=	$CH_3SCH_2CH_3$	$CH_3SCH_2CH_2$(—H)
33.2		52.1		-14.5	33.2+52.1-(-14.5) = 99.7

Bond energies:

CH_2(--H)SCH_2CH_3	**92.8 kcal/mol**
CH_3SCH(--H)CH_3	**92.5kcal/mol**
$CH_3SCH_2CH_2$--H	**99.7 kcal/mol**

3.2.3 X—H Bond Energies (X=C,O)

Bond energies corresponding to the loss of a H atom from the targeted C or O atom site on each parent molecule are reported at 298 K and 1 atm. The calculation are illustrated in Table 3.2 above where the radical $\Delta_f H^o(298)$ value is obtained from different work reactions for each species. Bond energies for the formation of radicals reported at 298 K are calculated from the absolute ΔH^o_{f298} values of the parent molecules and radicals are from the average CBS-QB3 level calculations. The work reactions here use the corresponding $\Delta_f H^o(298)$ of the radical and the parent and that of the hydrogen atom, 52.1 kcal/mol. The C—H bond energies of the parent molecules are summarized in Table 3.3 and Table 3.4. The ΔHrxn of the reaction below is used to define the bond energy:

$$\Delta_f H^o(298)\ \text{Parent} = \Delta_f H^o(298)\ \text{Radical} + \text{H atom}\ (52.1)$$

The bond energies of H—$CH_2SCH_2CH_3$, CH_3SCH(--H)CH_3 and $CH_3SCH_2CH_2$--H are calculated respectively using the reactions below:

$CH_3SCH_2CH_3 \rightarrow$ H• + $CH_2jSCH_2CH_3$

$CH_3SCH_2CH_3 \rightarrow$ H• + $CH_3SCHjCH_3$

and $CH_3SCH_2CH_3 \rightarrow$ H• + $CH_3SCH_2CH_2$, respectively

The values are 92.8, 92.5 and 99.7kcal/mol respectively, as shown in Table 3.3.

In Table 3.4, similar work reactions and methods were applied to calculate the targeted C—H or OO—H bond energies of the species containing one C–OOH group in each molecule. It's evident that in each molecule the H—X (X=C, O) bond on the peroxide group is the weakest, at the same time that on the carbon farthest to sulfur is the highest.

Table 3.4 H—X (X=C,O) Bond Energies of HOOCH$_2$SCH$_2$CH$_3$, CH$_3$SCH(OOH)CH$_3$ and CH$_3$SCH$_2$CH$_2$OOH Calculated in kcal/mol

					Bond Energy
•OOCH$_2$SCH$_2$CH$_3$	+	H•	=	HOOCH$_2$SCH$_2$CH$_3$	H--OOCH$_2$SCH$_2$CH$_3$
-1.8		52.1		-35.8	-1.8+52.1-(-35.8) = 86.1
HOOCH$_2$SC•HCH$_3$	+	H•	=	HOOCH$_2$SCH$_2$CH$_3$	HOOCH$_2$SCH(--H)CH$_3$
4.9		52.1		-35.8	4.9+52.1-(-35.8) = 92.8
HOOCH$_2$SCH$_2$C•H$_2$	+	H•	=	HOOCH$_2$SCH$_2$CH$_3$	HOOCH$_2$SCH$_2$CH$_2$(--H)
10.5		52.1		-35.8	10.5+52.1-(-35.8) = 98.4
C•H$_2$SCH(OOH)CH$_3$	+	H•	=	CH$_3$SCH(OOH)CH$_3$	CH$_2$(--H)SCH(OOH)CH$_3$
3.8		52.1		-39.9	3.8+52.1-(-39.9) = 95.8
CH$_3$SCH(OO•)CH$_3$	+	H•	=	CH$_3$SCH(OOH)CH$_3$	CH$_3$SCH(OO--H)CH$_3$
-5.1		52.1		-39.9	-5.1+52.1-(-39.9) = 86.9
CH$_3$SCH(OOH)C•H$_2$	+	H•	=	CH$_3$SCH(OOH)CH$_3$	CH$_3$SCH(OOH)CH$_2$(--H)
11.7		52.1		-39.9	11.7+52.1-(-39.9) = 103.7
C•H$_2$SCH$_2$CH$_2$OOH	+	H•	=	CH$_3$SCH$_2$CH$_2$OOH	CH$_2$(--H)SCH2CH2OOH
8.3		52.1		-34.2	8.3+52.1-(-34.2) = 94.6
CH$_3$SC•HCH$_2$OOH	+	H•	=	CH$_3$SCH$_2$CH$_2$OOH	CH$_3$SCH(--H)CH$_2$OOH
3.9		52.1		-34.2	3.9+52.1-(-34.2) = 90.2
CH$_3$SCH$_2$CH$_2$OO•	+	H•	=	CH$_3$SCH$_2$CH$_2$OOH	CH$_3$SCH$_2$CH$_2$OO—H
-0.3		52.1		-34.2	-0.3+52.1-(-34.2) = 86.0

Bond energies:

H--OOCH$_2$SCH$_2$CH$_3$	HOOCH$_2$SCH(--H)CH$_3$	HOOCH$_2$SCH$_2$CH$_2$(--H)	
86.1	92.8	98.4	kcal/mol
CH$_2$(--H)SCH(OOH)CH$_3$	CH$_3$SCH(OO--H)CH$_3$	CH$_3$SCH(OOH)CH$_2$(--H)	
95.8	86.9	103.7	kcal/mol
CH$_2$(--H)SCH2CH2OOH	CH$_3$SCH(--H)CH$_2$OOH	CH$_3$SCH$_2$CH$_2$OO—H	
94.6	90.2	86.0	kcal/mol

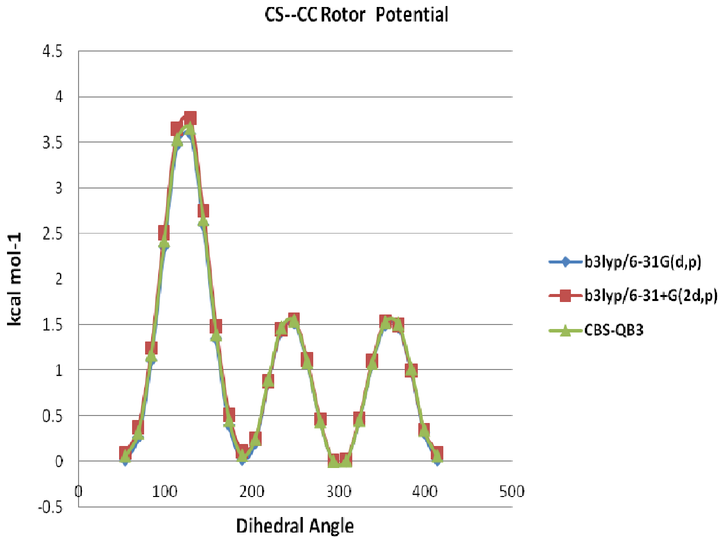
3.2.4 Frequencies and Moment of Inertia

The frequencies and the moments of inertia of the parent molecules and the corresponding radicals studied in Chapter 3 are listed in Table A.2 and Table A.3 in Appendix A. These parameters are needed for calculation of the thermo chemical properties at different temperatures and for frequencies and rotational spectroscopic constants as in FTIR and microwave analysis. Also, they're from the highest CQS-QB3 output files of the corresponding species.

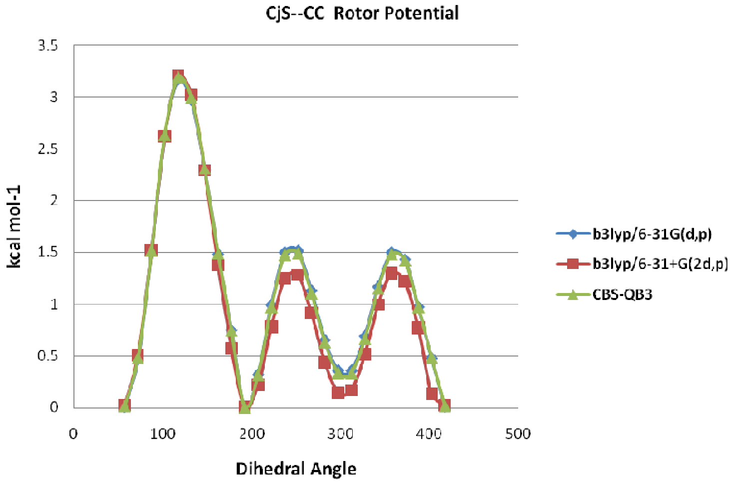
3.2.5 Internal Rotational Potentials

Figure 3.9-3.22 illustrate the internal rotor potentials of the parent molecule and their corresponding radicals of Methyl Ethyl Sulfide itself and all its presumed oxidation intermediates. They are also required when determining the lowest energy configuration of each molecule. The internal rotation potentials also indicate the relative energies and barriers to conversion between the conformers. They are also used to determine the entropy and heat capacity contributors from the internal rotors. Same to in Chapter 2, the energy as a function of rotation about the dihedral angle was computed by scanning the angle from 0° to 360^{o} in steps of 15^{o}.

In Figure 3.9 (a), (b), (c) and (d), those for $CH_3SCH_2CH_3$, $CH_2jSCH_2CH_3$, $CH_3SCHjCH_3$ and $CH_3SCH_2CH_2j$ are optimized using density functional theory at all the levels of B3LYP/6-31G(d,p), B3LYP/6-31+G(2d,p) and CBS-QB3.

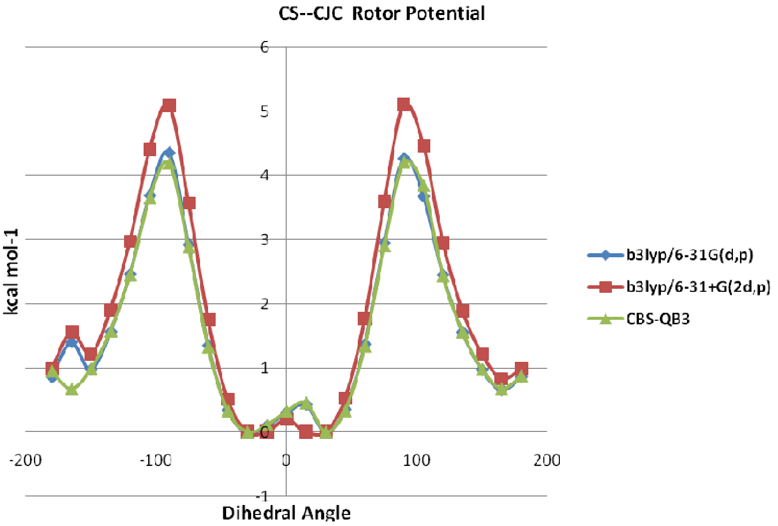


(a) CH_3S--CH_2CH_3

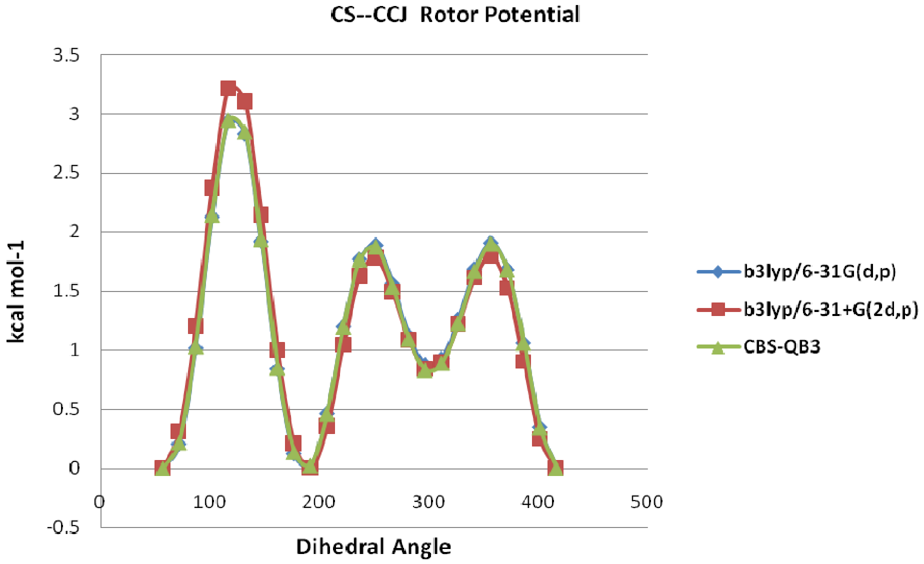


(b) CH_2jS--CH_2CH_3

Figure 3.9 Potential energy barriers for internal rotations of the CS—CC bond in $CH_3SCH_2CH_3$, $CH_2jSCH_2CH_3$, $CH_3SCHjCH_3$ and $CH_3SCH_2CH_2j$ at B3LYP/6-31G(d, p) , B3LYP/6-31+G (2d, p) and CBS-QB3 level.



(c) CH_3S--$CHjCH_3$

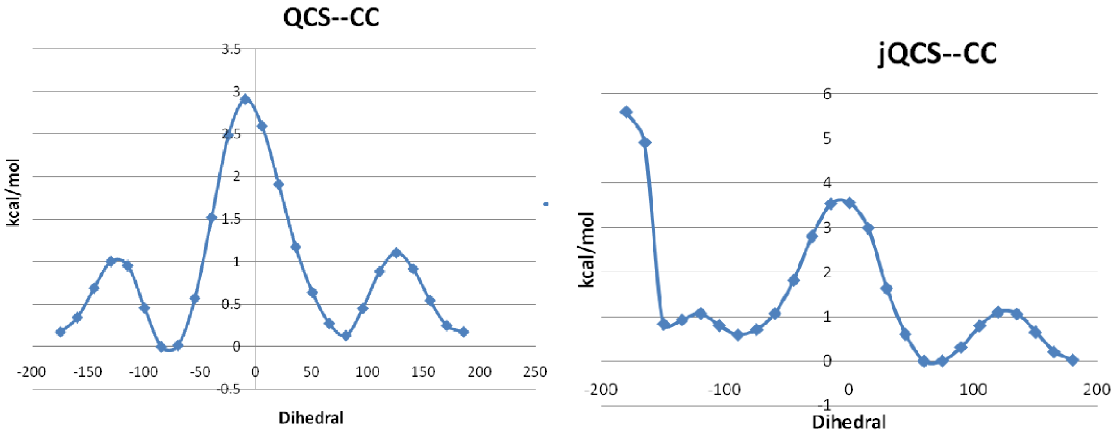


(d) CH_3S--CH_2CH_2j

Figure 3.9 Potential energy barriers for internal rotations of the CS—CC bond in $CH_3SCH_2CH_3$, $CH_2jSCH_2CH_3$, $CH_3SCHjCH_3$ and $CH_3SCH_2CH_2j$ at B3LYP/6-31G(d, p) , B3LYP/6-31+G (2d, p) and CBS-QB3 level. (Continued)

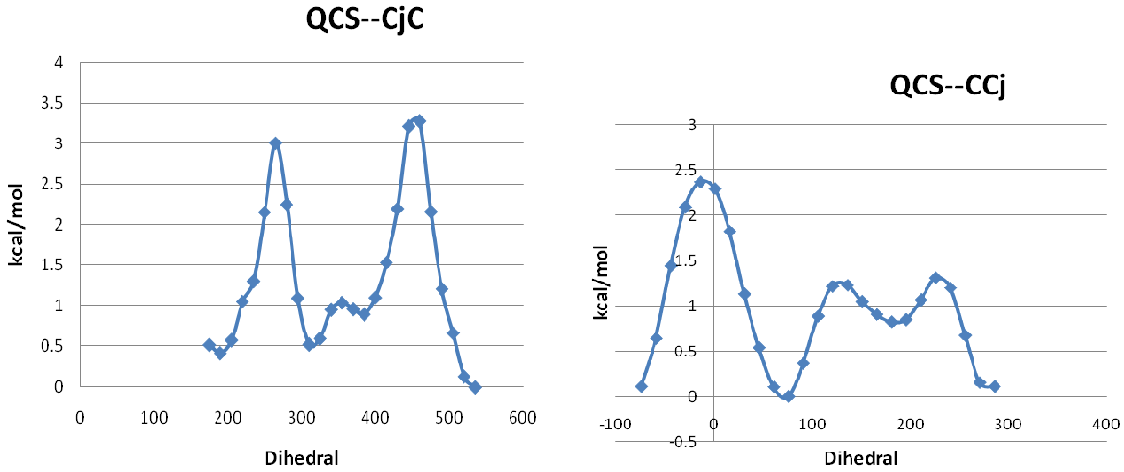
As three different levels of calculation outputs can be considered to be in an acceptable agreement with each other, so in the following targeted rotors, only the internal rotor potentials under the level of B3LYP/6-31g(d) were discussed for the molecules containing one peroxide group in each molecule and their radicals, as shown in Figure 3.10 -3.18.

In Figure 3.10-3.12 there are rotation barriers of the bond between the sulfur and the secondary carbon atom , in each molecule and radical containing the peroxide group.



(a) $HOOCH_2S—CH_2CH_3$

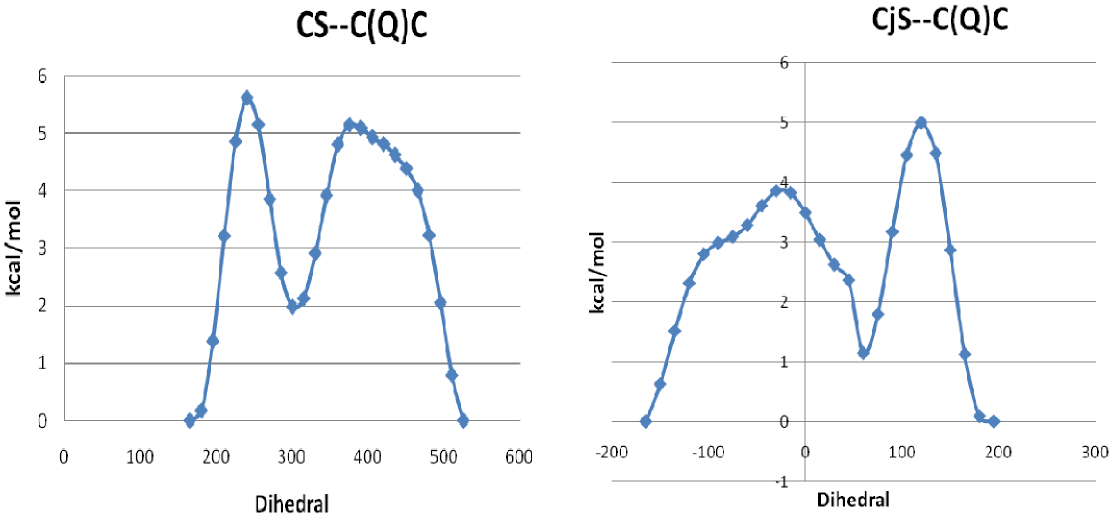
(b) $jOOCH_2S—CH_2CH_3$



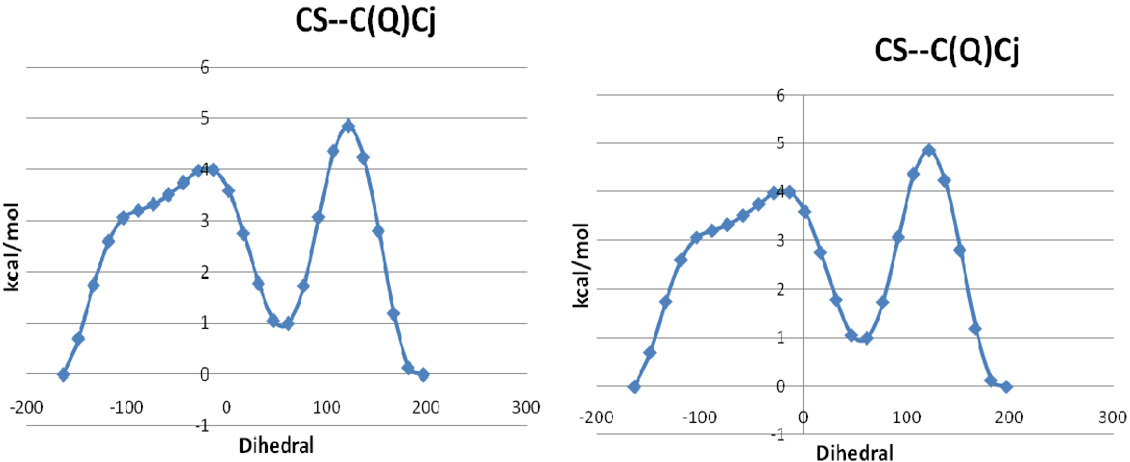
(c) $HOOCH_2S—CHjCH_3$

(d) $HOOCH_2S—CH_2CH_2j$

Figure 3.10 Potential energy barriers for internal rotations of the QCS—CC ($HOOCH_2S—CH_2CH_3$) bonds in QCS—CC ($HOOCH_2S—CH_2CH_3$), jQCS—CC ($jOOCH_2S—CH_2CH_3$), QCS—CjC ($HOOCH_2S—CHjCH_3$) and QCS—CCj ($HOOCH_2S—CH_2CH_2j$) at B3LYP/6-31G(d) level.

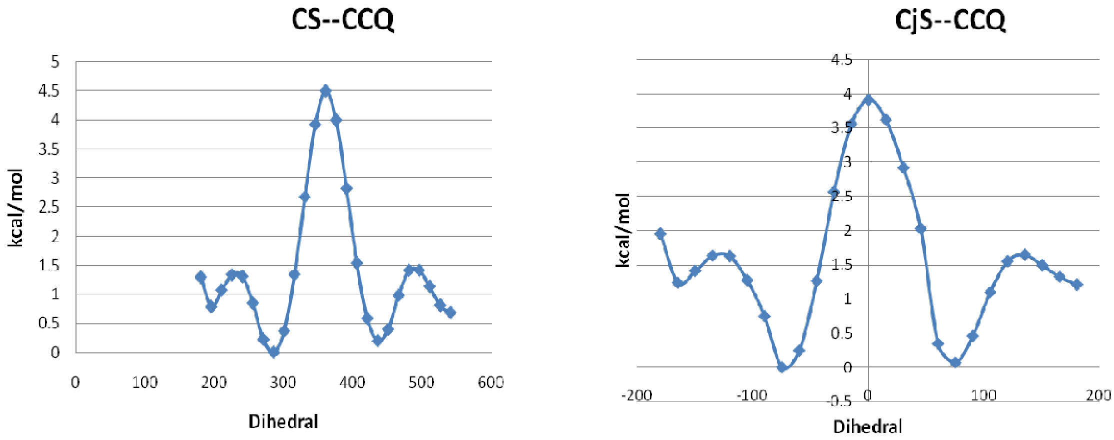


(a) $CH_3S—CH(OOH)CH_3$ (b) $CH_2jS—CH(OOH)CH_3$

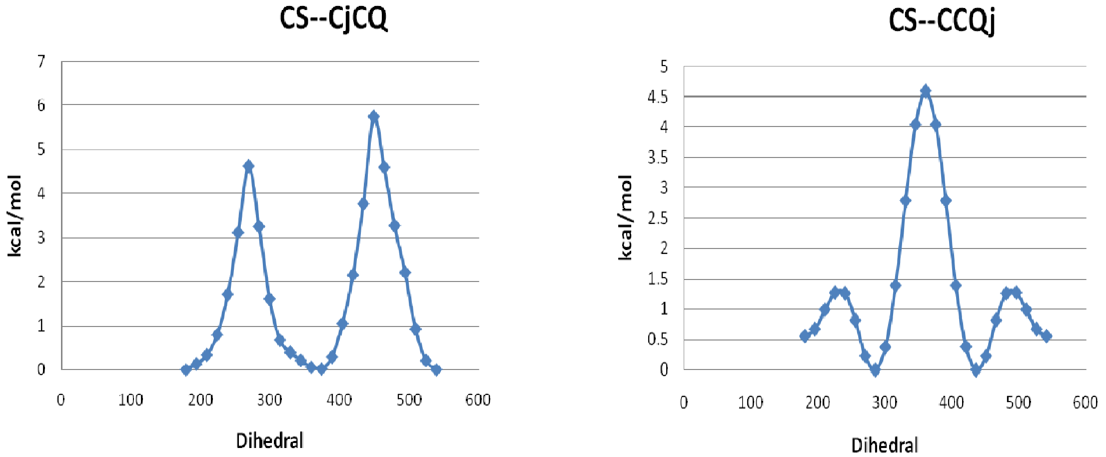


(c) $CH_3S—CH(OOj)CH_3$ (d) $CH_3S—CH(OOH)CH_2j$

Figure 3.11 Potential energy barriers for internal rotations of the CS—C(Q)C ($CH_3S—CH(OOH)CH_3$) bonds in CS—C(Q)C ($CH_3S—CH(OOH)CH_3$), CjS—C(Q)C ($CH_2jS—CH(OOH)CH_3$), CS—C(Qj)C ($CH_3S—CH(OOj)CH_3$) and CS—C(Q)Cj ($CH_3S—CH(OOH)CH_2j$) at B3LYP/6-31G(d) level.



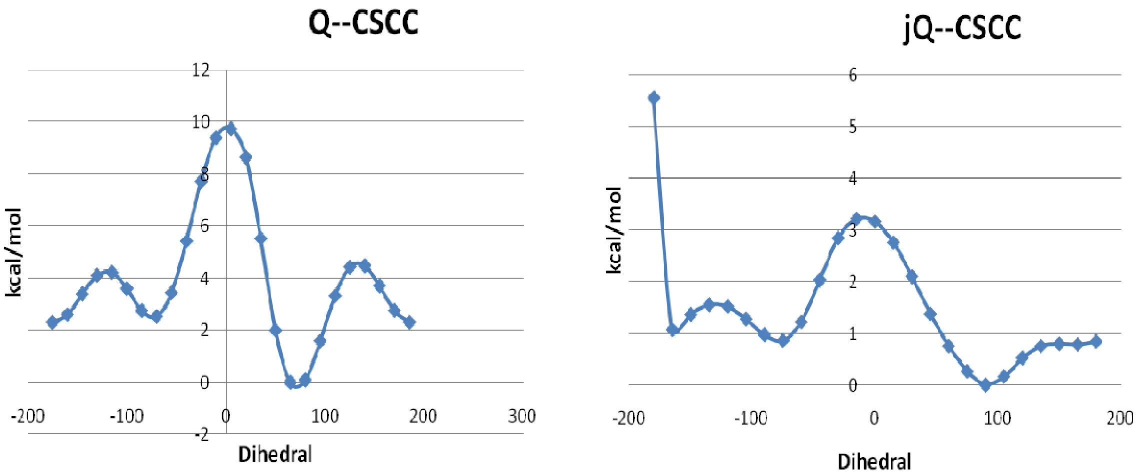
(a) $CH_3S—CH_2CH_2OOH$ (b) $CH_2jS—CH_2CH_2OOH$



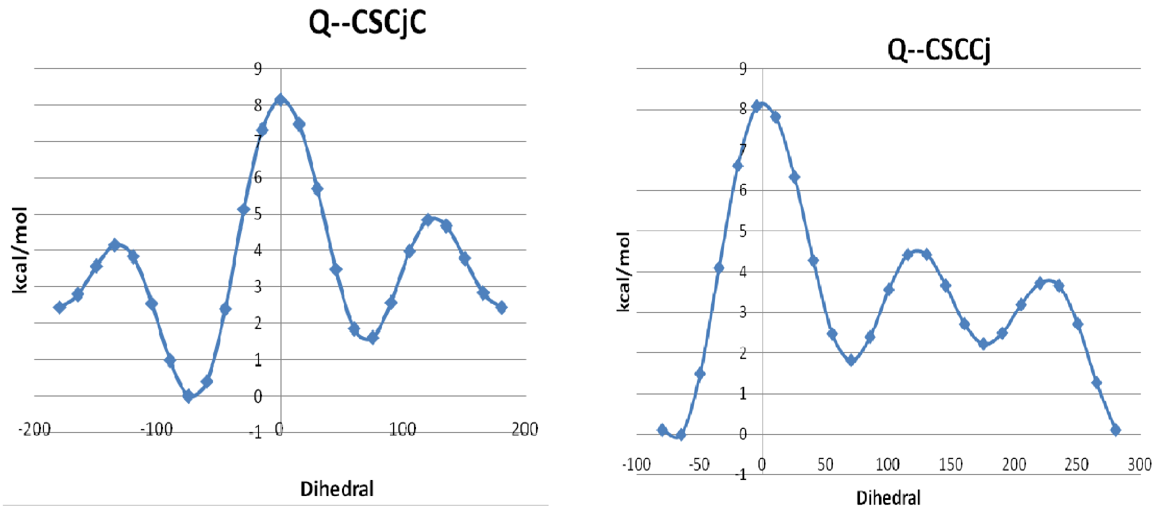
(c) $CH_3S—CH_2jCH_2OOH$ (d) $CH_3S—CH_2CH_2OOj$

Figure 3.12 Potential energy barriers for internal rotations of the CS—CCQ ($CH_3S—CH_2CH_2OOH$) bonds in CS—CCQ ($CH_3S—CH_2CH_2OOH$), CjS—CCQ ($CH_2jS—CH_2CH_2OOH$), CS—CjCQ ($CH_3S—CH_2jCH_2OOH$) and CS—CCQj ($CH_3S—CH_2CH_2OOj$) at B3LYP/6-31G(d) level.

Then, in Figure 3.13-3.15, there are rotational barriers of the bond connecting the peroxide group to the carbon atom in each molecule and radical containing the peroxide group.

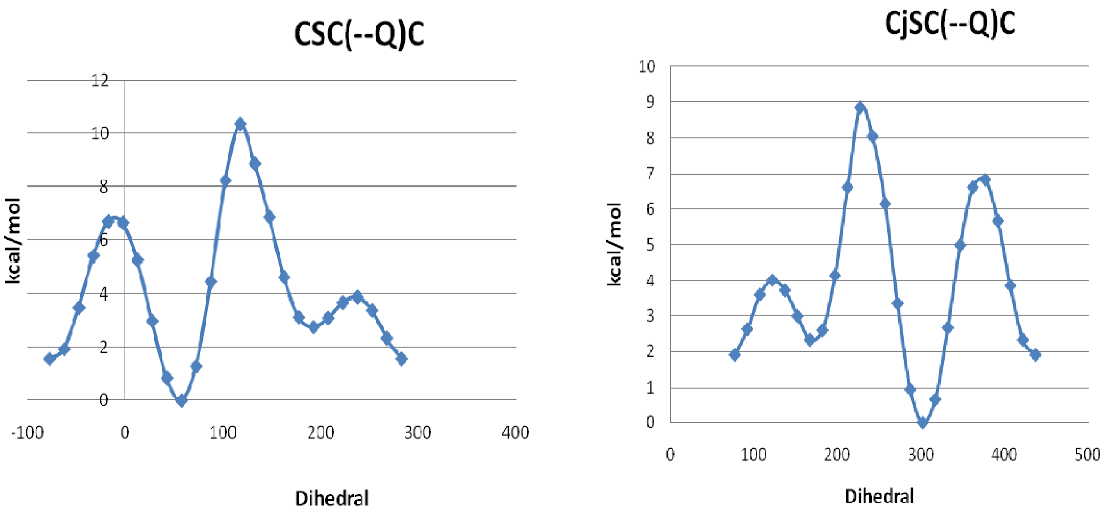


(a) HOO—$CH_2SCH_2CH_3$ (b) jOO—$CH_2SCH_2CH_3$

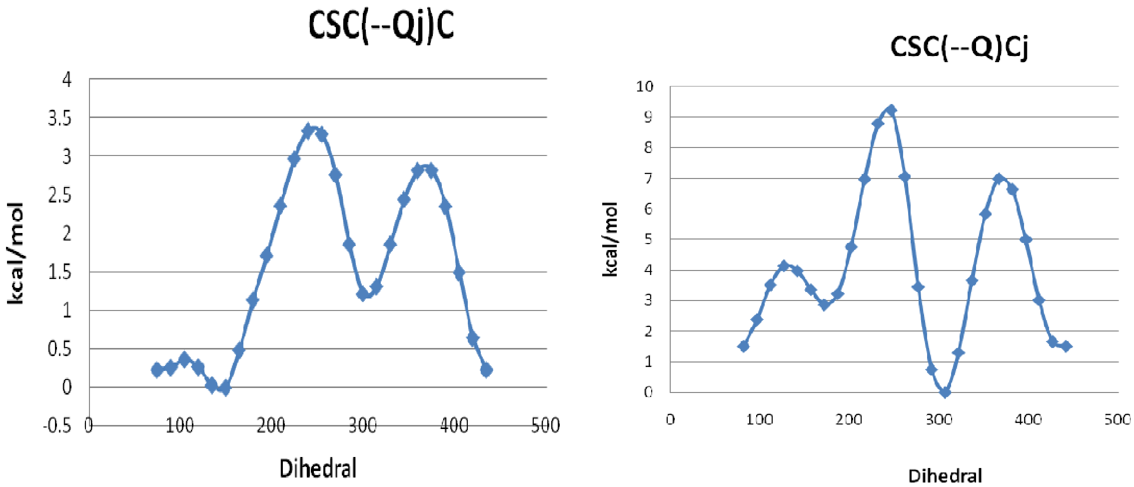


(c) HOO—$CH_2SCHjCH_3$ (d) HOO—$CH_2SCH_2CH_2j$

Figure 3.13 Potential energy barriers for internal rotations of the C--Q bonds in Q—CSCC (HOO—$CH_2SCH_2CH_3$), jQ—CSCC (jOO—$CH_2SCH_2CH_3$), Q—CSCjC (HOO—$CH_2SCHjCH_3$) and Q—CSCCj (HOO—$CH_2SCH_2CH_2j$) at B3LYP/6-31G(d) level.

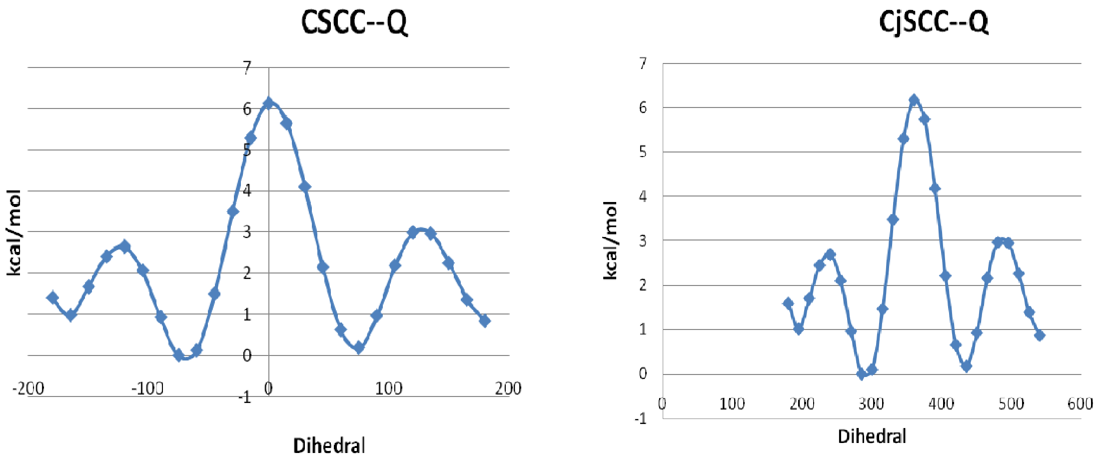


(a) $CH_3SCH(—OOH)CH_3$ (b) $CH_2jSCH(—OOH)CH_3$



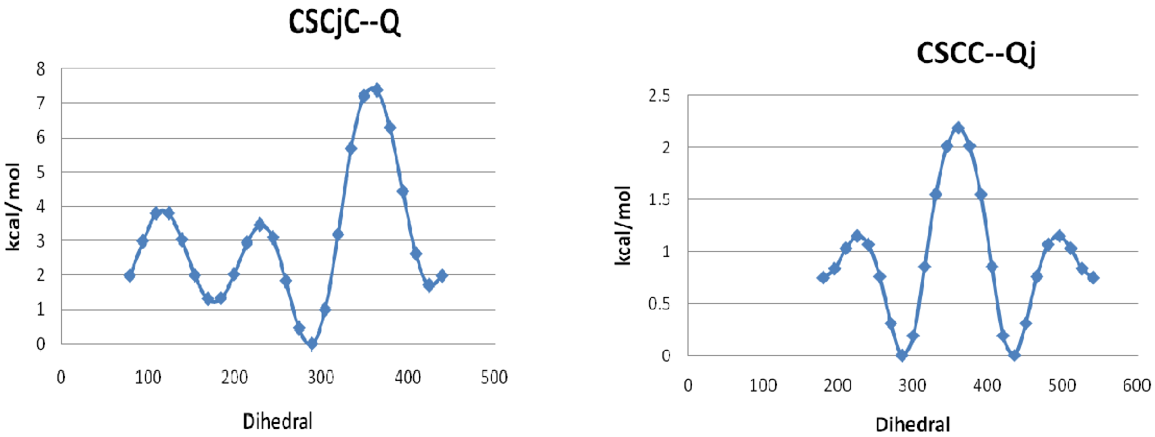
(c) $CH_3SCH(—OOj)CH_3$ (d) $CH_3SCH(—OOH)CH_2j$

Figure 3.14 Potential energy barriers for internal rotations of the C--Q bonds in CSC(--Q)C ($CH_3SCH(—OOH)CH_3$), CjSC(—Q)C ($CH_2jSCH(—OOH)CH_3$), CSC(—Qj)C ($CH_3SCH(—OOj)CH_3$) and CSC(—Q)Cj ($CH_3SCH(—OOH)CH_2j$) at B3LYP/6-31G(d) level.



(a) $CH_3SCH_2CH_2$—OOH

(b) $CH_2jSCH_2CH_2$—OOH

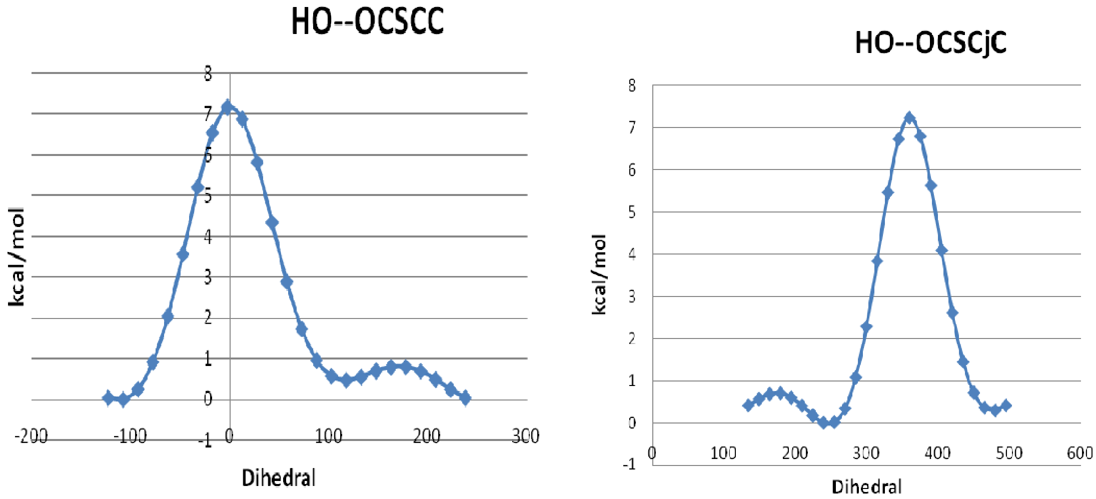


(c) $CH_3SCHjCH_2$—OOH

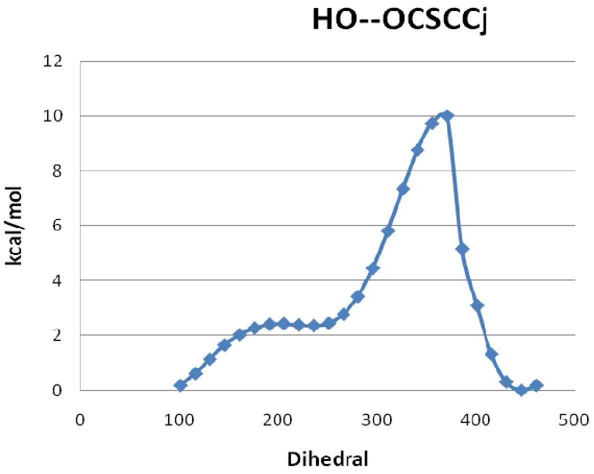
(d) $CH_3SCH_2CH_2$—OOj

Figure 3.15 Potential energy barriers for internal rotations of the C--Q bonds in CSCC—Q ($CH_3SCH_2CH_2$—OOH), CjSCC—Q ($CH_2jSCH_2CH_2$—OOH), CSCjC—Q ($CH_3SCHjCH_2$—OOH) and CSCC—Qj ($CH_3SCH_2CH_2$—OOj) at B3LYP/6-31G(d) level.

And then, in Figure 3.16-3.18, there are rotation barriers of the bond between the two oxygen atoms on the hydrogen peroxide group, for each molecule and radical with a complete hydrogen peroxide group attached to one carbon atom in the molecule.

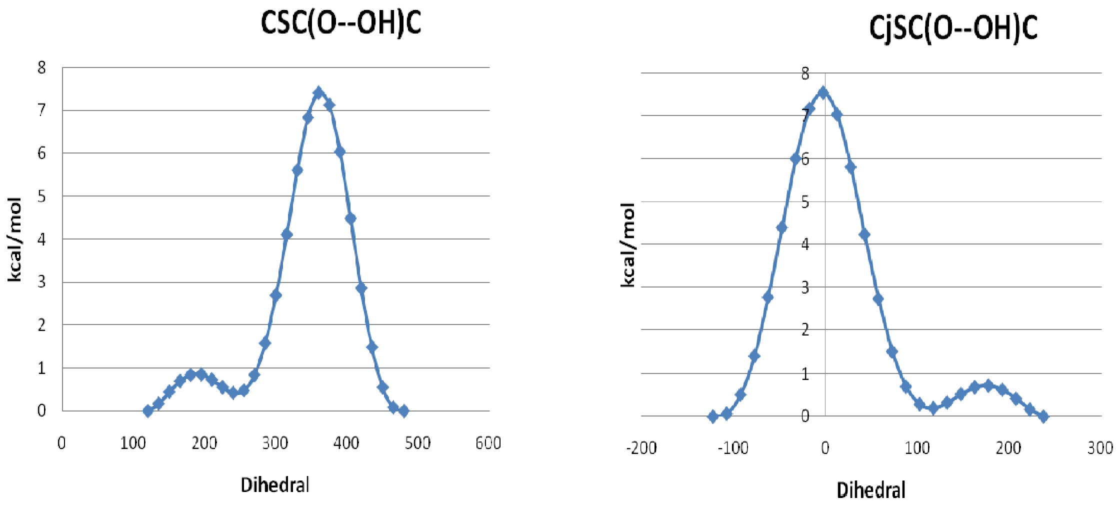


(a) HO—$OCH_2SCH_2CH_3$ (b) HO—$OCH_2SCHjCH_3$



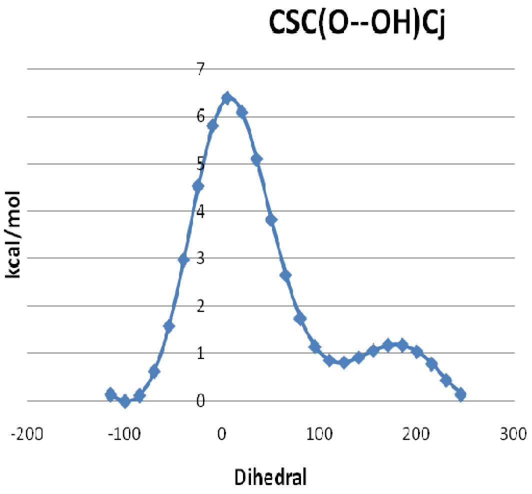
(c) HO—$OCH_2SCH_2CH_2j$

Figure 3.16 Potential energy barriers for internal rotations of the CO--OH bonds in HO--OCSCC (HO—$OCH_2SCH_2CH_3$), HO—OCSCjC (HO—$OCH_2SCHjCH_3$) and HO--OCSCCj (HO—$OCH_2SCH_2CH_2j$) at B3LYP/6-31G(d) level.



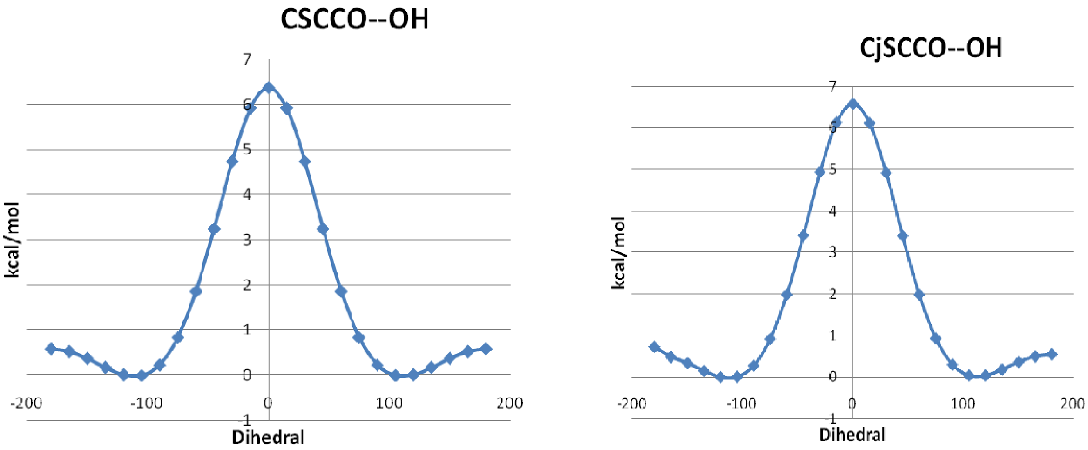
(a) $CH_3SCH(O—OH)CH_3$

(b) $CH_2jSCH(O—OH)CH_3$

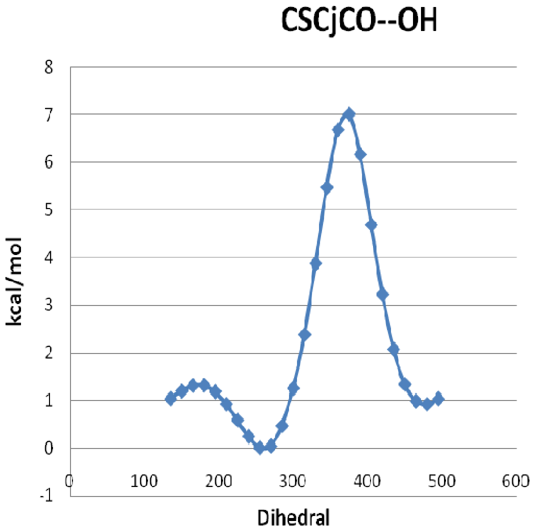


(c) $CH_3SCH(O—OH)CH_2j$

Figure 3.17 Potential energy barriers for internal rotations of the CO--OH bonds in CSC(O--OH)C ($CH_3SCH(O—OH)CH_3$), CjSC(O—OH)C ($CH_2jSCH(O—OH)CH_3$) and CSC(O--OH)Cj ($CH_3SCH(O—OH)CH_2j$) at B3LYP/6-31G(d) level.



(a) $CH_3SCH_2CH_2O$—OH (b) $CH_2jSCH_2CH_2O$—OH



(c) $CH_3SCHjCH_2O$—OH

Figure 3.18 Potential energy barriers for internal rotations of the CO--OH bonds in CSCCO—OH ($CH_3SCH_2CH_2O$—OH), CjSCCO—OH ($CH_2jSCH_2CH_2O$—OH) and CSCjCO—OH ($CH_3SCHjCH_2O$—OH) at B3LYP/6-31G(d) level.

Then, the internal rotor potentials optimized under the level of B3LYP/6-31g(2d,2p) for the targeted bonds in the stable molecules of $CH_3S(=O)CH_2OH$ and $CH_3S(=O)CH(OH)CH_3$ were also discussed, and they're shown in Figure 3.19-3.22.Same as in Chapter 2, all scans are performed in relaxed mode.

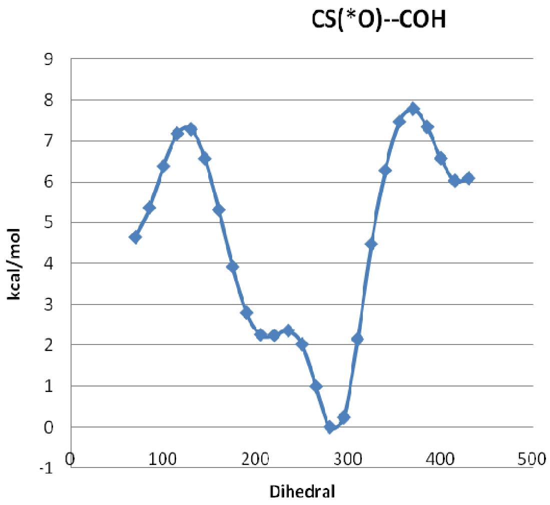


Figure 3.19 Potential energy barriers for internal rotation of the CS(=O)--COH bond in $CH_3S(=O)CH_2OH$ at B3LYP/6-31G(2d,2p) level.

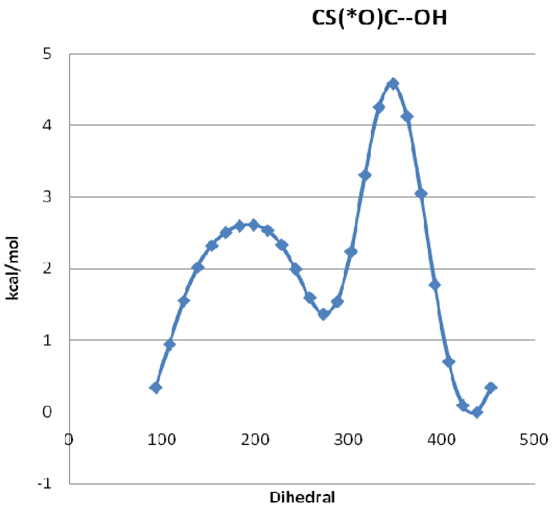


Figure 3.20 Potential energy barriers for internal rotation of the CS(=O)C--OH bond in $CH_3S(=O)CH_2OH$ at B3LYP/6-31G(2d,2p) level.

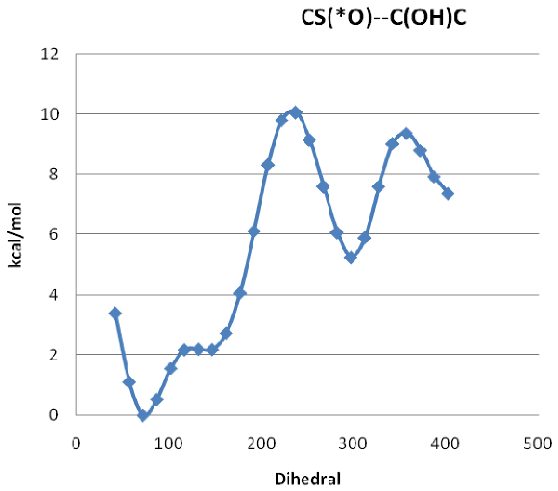


Figure3.21 Potential energy barriers for internal rotation of the CS(=O)--C(OH)C bond in CH3S(=O)CH(OH)CH_3 at B3LYP/6-31G(2d,2p) level.

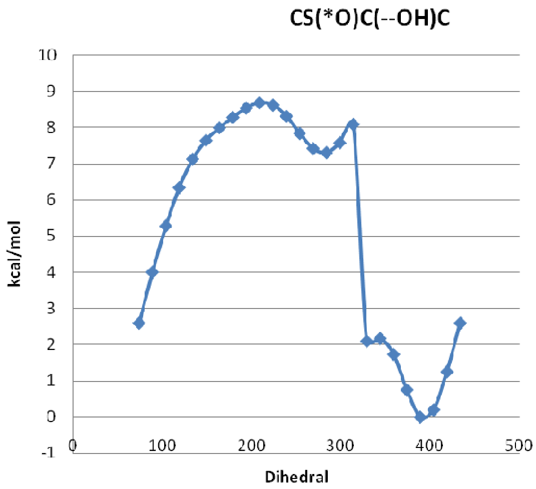


Figure 3.22 Potential energy barriers for internal rotation of the CS(=O)C(--OH)C bond in CH3S(=O)CH(OH)CH_3 at B3LYP/6-31G(2d,2p) level.

3.2.6 S°298 and Cp°(T)

Entropy and heat capacity values from vibration, translation and rotation contributions are calculated using SMCPS and the Rotator programs. The scaled vibrations and the moment of inertia are from the optimized geometries under the B3LYP/6-31G(2d,d,p) in the CBS-QB3 method. These are scaled by the factor of 0.9613. Table 3.5 lists the data about 298K entropy and heat capacity vs. temperature of all the parents and radicals accompanied by those of their radicals after one H atom departure. Then, the ideal gas-phase thermodynamic property vs. temperature data of each species are listed in Table B.4-B.8 in Appendix B, with a temperature range of 1-5000K. All these data are also ideal gas thermodynamic properties at standard state (P=1atm and T=298K). To note, same as that mentioned in section 2.2.6, torsion frequencies are used for internal rotor contribution, with the ROTOR in the SMCPS input files being 0.

Table 3.5 298K Entropy, and Data of Heat Capacity vs. Temperature

Species	S°_{298K}	Cp 300	Cp 400	Cp 500	Cp 600	Cp 800	Cp 1000	Cp 1500
CSCC	76.7	22.3	27.5	32.4	36.5	43.2	48.2	56.2
CjSCC	74.8	22.8	27.6	31.8	35.3	40.9	45.1	51.8
CSCjC	76.4	22.6	27.2	31.4	35.0	40.7	45.0	51.8
CSCCj	75.9	23.0	27.8	32.0	35.5	41.0	45.2	51.9
CQSCC	93.2	29.9	36.3	41.9	46.6	53.9	59.2	67.5
CQjSCC	93.9	27.9	33.9	39.2	43.6	50.5	55.4	63.0
CQSCjC	94.5	30.5	36.2	41.1	45.2	51.4	56.0	63.2
CQSCCj	90.1	30.4	36.5	41.5	45.6	51.7	56.2	63.2
CSCQC	87.2	30.8	37.1	42.5	47.1	54.2	59.4	67.6
CjSCQC	87.2	31.2	37.1	41.9	45.9	51.8	56.2	63.2
CSCQjC	88.1	28.7	34.6	39.8	44.1	50.7	55.6	63.1
CSCQCj	88.8	31.6	37.4	42.2	46.1	52.0	56.4	63.3
CSCCQ	85.4	26.1	32.2	37.8	42.5	49.8	55.2	63.5
CjSCCQ	91.5	30.6	36.3	41.2	45.3	51.5	56.0	63.1
CSCjCQ	91.9	30.0	35.9	40.9	45.0	51.3	55.9	63.1
CSCCQj	91.1	27.8	33.7	39.1	43.5	50.4	55.4	63.0
CSCOH	70.9	17.3	21.4	25.1	28.3	33.3	37.0	42.9
CCSCOH	79.9	25.6	31.6	36.9	41.4	48.3	53.5	61.7
CS(=O)COH	79.9	24.8	29.7	33.9	37.4	42.7	46.6	52.6
CS(=O)C(OH)C	84.2	29.5	36.2	41.9	46.7	54.0	59.3	67.6

3.3 Summary

Structures, thermochemical parameters Hf, S, Cp(t), bond energies, internal rotor potentials, vibration frequencies properties and molecular structures are presented for the lowest energy conformers of parent $CH_3SCH_2CH_3$ and three of its main partial oxidation intermediates with one attached hydrogen peroxide group: $HOOCH_2SCH_2CH_3$, $CH_3SCH(OOH)CH_3$ and $CH_3SCH_2CH_2OOH$, and three radicals on each of them corresponding to loss of an H atom from one C or O atom in the molecule. The corresponding alcohols and sulfoxide intermediates have also been studied. They were calculated using density functional theory and the composite CBS-QB3 methods. Enthalpies from all the work reactions and each of the calculation levels can be considered to be in reasonably good agreement. The CBS-QB3 results are recommended as these are the highest calculation level. It’s evident that B3LYP/6-31G+(2d,p) calculations are an acceptable method for larger sulfur-oxygen hydrocarbons when used together with several work reactions.

APPENDIX A

FREQUENCIES AND MOMENTS OF INERTIA FROM CBS-QB3 OUTPUT FILES

Lists the frequencies and the moments of inertia of the parent molecules and the corresponding radicals. They are needed for SMCPS calculation of thermochemical properties of the corresponding species.

Table A.1 Frequencies and Moments of Inertia from CBS-QB3 Output Files of Stable CH_3SCH_2CHO, CH_3CH_2SCHO and $CH_3SC(=O)CH_3$ and Their Radicals Formed After Losing One H Atom.

Species	Moments of Inertia, units amu $(Bohr)^2$	Frequencies (cm^{-1})
CH_3SCH_2CHO	259.8 665.6 835.9	88, 116, 169, 265, 303, 492, 657, 707, 861, 939, 983, 1033, 1049, 1187, 1231, 1365, 1412, 1448, 1467, 1486, 1797, 2897, 3043, 3058, 3124, 3128, 3136
CH_2jSCH_2CHO	226.1 683.1 836.6	72, 114, 190, 267, 318, 388, 483, 662, 816, 849, 923, 1021, 1037, 1184, 1231, 1402, 1412, 1445, 1805, 2900, 3059, 3131, 3154, 3283
$CH_3SCHjCHO$	257.1 565.5 811.3	71, 170, 216, 294, 325, 661, 668, 709, 810, 958, 967, 1004, 1108, 1360, 1380, 1415, 1457, 1461, 1606, 2906, 3063, 3156, 3175, 3175
CH_3SCH_2CjO	268.2 626.0 784.6	89, 157, 180, 204, 265, 581, 678, 715, 765, 796, 978, 996, 1173, 1246, 1357, 1405, 1467, 1490, 1935, 3039, 3042, 3105, 3123, 3140
CH_3CH2_SCHO	317.4 564.0 783.8	63, 196, 230, 278, 346, 515, 640, 734, 776, 933, 980, 1069, 1078, 1286, 1307, 1372, 1415, 1459, 1494, 1504, 1756, 2943, 3032, 3067, 3094, 3110, 3130
CH_2jCH_2SCHO	316.0 527.9 752.7	72, 200, 221, 274, 318, 512, 525, 647, 729, 768, 930, 1048, 1077, 1227, 1271, 1368, 1445, 1475, 1752, 2941, 3074, 3135, 3148, 3258
$CH_3CHjSCHO$	190.9 742.9 922.1	70, 91, 168, 263, 330, 445, 535, 687, 762, 885, 1002, 1030, 1112, 1303, 1362, 1412, 1474, 1487, 1745, 2964, 2971, 3046, 3087, 3197
CH_3CH_2SCjO	315.2 556.2 780.7	65, 154, 254, 276, 349, 478, 578, 612, 767, 976, 1054, 1073, 1274, 1291, 1418, 1463, 1494, 1503, 1842, 3032, 3058, 3094, 3105, 3125
$CH_3SC{=}OCH_3$	247.4 590.8 815.5	26, 42, 136, 211, 350, 484, 540, 612, 710, 954, 981, 1007, 1018, 1126, 1354, 1388, 1461, 1470, 1474, 1476, 1776, 3041, 3059, 3110, 3130, 3151, 3153
$CH_2jSC{=}OCH_3$	234.5 570.1 793.5	45, 143, 235, 254, 355, 380, 474, 523, 600, 821, 922, 990, 1013, 1120, 1371, 1391, 1468, 1476, 1783, 3040, 3105, 3130, 3158, 3299
$CH_3SC{=}OCH_2j$	242.9 555.3 786.8	55, 119, 214, 349, 354, 472, 552, 616, 713, 737, 969, 978, 1020, 1156, 1354, 1453, 1458, 1470, 1654, 3057, 3148, 3148, 3152, 3267

Table A.2 Frequencies and Moments of Inertia From CBS-QB3 Output Files of Stable $CH_3SCH_2CH_3$, $HOOCH_2SCH_2CH_3$, $CH_3SCH(OOH)CH_3$ and $CH_3SCH_2CH_2OOH$ and Their Radicals Formed After Losing One H Atom.

Species	Moments of Inertia, units amu (Bohr)^2	Frequencies (cm^{-1})
$CH_3SCH_2CH_3$	186.5 475.2 578.2	90, 172, 208, 277,350, 638, 709, 761, 960, 973, 980, 1063, 1084, 1281, 1303, 1360, 1413, 1466, 1473, 1485, 1495, 1502, 3025, 3034, 3038, 3078, 3087, 3109, 3113, 3126
$CH_2jSCH_2CH_3$	166.9 459.0 546.7	101, 211, 240, 282, 363, 418, 641, 767, 828, 924, 976, 1062, 1080, 1277, 1301, 1404, 1413, 1471, 1490, 1502, 3028, 3046, 3089, 3093, 3115, 3139, 3265
$CH_3SCHjCH_3$	183.3 424.5 573.5	94, 149, 201, 235, 386, 440, 670, 733, 960, 974, 1008, 1045, 1103, 1316, 1357, 1408, 1468, 1476, 1486, 1490, 2951, 3041, 3046, 3086, 3127, 3134, 3172
$CH_3SCH_2CH_2j$	186.1 444.2 550.8	95, 166, 207, 258, 319, 546, 626, 702, 761, 953, 974, 1063, 1071, 1224, 1264, 1356, 1454, 1469, 1480, 1486, 3035, 3046, 3098, 3115, 3128, 3142, 3245
$HOOCH_2SCH_2CH_3$	265.4 1412.5 1575.6	48, 74, 125, 204, 214, 241, 267, 324, 432, 658, 774, 796, 878, 946, 991, 1006, 1050, 1083, 1223, 1266, 1296, 1324, 1357, 1417, 1490, 1493, 1496, 1506, 3023, 3032, 3048, 3079, 3091, 3098, 3118, 3772
$jOOCH_2SCH_2CH_3$	277.3 1330.9 1510.1	15, 57, 108, 199, 241, 274, 351, 453, 656, 776, 797, 864, 914, 990, 1050, 1079, 1159, 1219, 1269, 1298, 1323, 1419, 1453, 1490, 1496, 1506, 3034, 3047, 3069, 3092, 3100, 3115, 3138
$HOOCH_2SCHjCH_3$	253.1 1410.4 1567.3	50, 68, 100, 122, 188, 216, 260, 329, 396, 444, 719, 773, 873, 953, 1006, 1012, 1037, 1110, 1223, 1298, 1321, 1363, 1412, 1473, 1488, 1493, 2959, 3027, 3041, 3082, 3084, 3167, 3777
$HOOCH_2SCH_2CH_2j$	473.1 820.3 1160.9	52, 94, 131, 209, 261, 298, 325, 359, 483, 534, 626, 689, 757, 862, 939, 1014, 1055, 1073, 1220, 1262, 1276, 1318, 1384, 1428, 1454, 1481, 3043, 3056, 3108, 3118, 3145, 3254, 3709
$CH_3SCH(OOH)CH_3$	422.0 924.4 1240.4	89, 120, 136, 196, 208, 249, 268, 333, 408, 475, 698, 730, 857, 881, 974, 978, 1033, 1090, 1119, 1271, 1344, 1354, 1368, 1404, 1466, 1486, 1490, 1499, 3040, 3045, 3047, 3113, 3117, 3127, 3148, 3781
$CH_2jSCH(OOH)CH_3$	395.6 905.9 1214.1	82, 124, 198, 203, 239, 257, 270, 340, 405, 454, 478, 714, 817, 861, 889, 936, 1030, 1088, 1119, 1265, 1348, 1372, 1396, 1405, 1486, 1499, 3041, 3064, 3114, 3118, 3152, 3280, 3781

Table A.2 Frequencies and Moments of Inertia From CBS-QB3 Output Files of Stable $CH_3SCH_2CH_3$, $HOOCH_2SCH_2CH_3$, $CH_3SCH(OOH)CH_3$ and $CH_3SCH_2CH_2OOH$ and Their Radicals Formed After Losing One H Atom. (Continued)

Species	Moments of Inertia, units amu (Bohr)^2	Frequencies (cm^{-1})
$CH_3SCH(OOj)CH_3$	429.0 871.1 1198.3	61, 98, 145, 184, 230, 287, 331, 435, 454, 698, 727, 802, 974, 979, 1007, 1082, 1109, 1169, 1281, 1336, 1359, 1409, 1468, 1486, 1488, 1495, 3045, 3045, 3087, 3122, 3123, 3130, 3143
$CH_3SCH(OOH)CH_2j$	407.2 920.4 1217.7	83, 116, 137, 187, 201, 228, 265, 318, 400, 481, 553, 692, 758, 861, 879, 974, 974, 1050, 1108, 1216, 1346, 1349, 1358, 1447, 1465, 1488, 3045, 3049, 3127, 3145, 3148, 3259, 3764
$CH_3SCH_2CH_2OOH$	144.6 1850.4 1960.7	-109, 38, 80, 116, 121, 185, 247, 318, 464, 704, 759, 818, 936, 972, 976, 1032, 1046, 1082, 1218, 1264, 1286, 1358, 1374, 1440, 1468, 1484, 1495, 1535, 3016, 3034, 3044, 3055, 3096, 3112, 3129, 3804
$CH_2jSCH_2CH_2OOH$	129.9 1806.3 1907.5	442, 78, 116, 129, 191, 211, 272, 317, 385, 478, 744, 811, 832, 930, 941, 1023, 1034, 1087, 1211, 1264, 1286, 1368, 1401, 1408, 1492, 1531, 3012, 3056, 3062, 3116, 3148, 3275, 3769
$CH_3SCHjCH_2OOH$	249.7 1441.7 1522.9	47, 59, 129, 162, 193, 217, 268, 418, 449, 598, 695, 755, 844, 942, 968, 974, 1032, 1121, 1257, 1327, 1354, 1362, 1369, 1457, 1468, 1482, 3014, 3044, 3070, 3128, 3139, 3186, 3774
$CH_3SCH_2CH_2OOj$	139.7 1799.7 1905.0	40, 70, 92, 123, 185, 258, 313, 508, 702, 761, 798, 945, 970, 981, 1015, 1090, 1185, 1186, 1266, 1292, 1360, 1392, 1469, 1483, 1495, 1504, 3037, 3043, 3064, 3090, 3116, 3124, 3132

Table A.3 Frequencies and Moments of Inertia From CBS-QB3 Output Files of Stable CH_3SCH_2OH, CH_3CH_2SCHO and $CH_3SC(=O)CH_3$.

Species	Moments of Inertia, units amu $(Bohr)^2$	Frequencies (cm^{-1})
CH_3SCH_2OH	106.1 553.1 636.1	-119, 111, 164, 203, 372, 703, 727, 952, 981, 988, 1079, 1214, 1221, 1356, 1401, 1468, 1485, 1519, 2970, 3010, 3029, 3100, 3128, 3834
$CH_3CH_2SCH_2OH$	307.1 722.6 859.5	65, 130, 193, 259, 337, 347, 458, 636, 682, 762, 921, 977, 1043, 1066, 1073, 1190, 1284, 1295, 1331, 1396, 1414, 1476, 1487, 1496, 1499, 3017, 3025, 3057, 3086, 3093, 3110, 3116, 3799
$CH_3S(=O)CH_2OH$	273.6 600.3 769.0	109, 185, 214, 283, 308, 366, 381, 632, 706, 880, 937, 991, 1065, 1080, 1150, 1299, 1327, 1380, 1454, 1468, 1489, 3034, 3037, 3117, 3137, 3148, 3826
$CH_3S(=O)CH(OH)CH_3$	429.0 816.1 853.7	95, 201, 212, 246, 278, 292, 350, 454, 506, 592, 635, 662, 902, 940, 953, 1015, 1028, 1112, 1148, 1204, 1325, 1353, 1410, 1453, 1456, 1470, 1490, 1496, 3031, 3040, 3069, 3104, 3108, 3138, 3152, 3493

APPENDIX B

IDEAL GAS-PHASE THERMODYNAMIC PROPERTY VS. TEMPERATURE DIRECTLY FROM SMCPS OUTPUT FILES

Entropy and heat capacity values from vibration, translation and rotation contributions that are calculated using SMCPS and the Rotor programs. And torsion frequencies are used for internal rotor contribution, with the ROTOR in the SMCPS input files being 0.

Table B.1 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of CH_3SCH_2CHO and its Radicals.

(a) CH_3SCH_2CHO

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	18.405	.008
50.00	10.444	50.512	.436
100.00	13.794	58.849	1.047
150.00	16.192	64.907	1.799
200.00	18.403	69.861	2.664
250.00	20.740	74.209	3.642
298.00	23.103	78.046	4.694
300.00	23.203	78.201	4.740
400.00	28.090	85.540	7.307
500.00	32.440	92.277	10.339
600.00	36.120	98.517	13.773
700.00	39.221	104.316	17.544
800.00	41.861	109.723	21.602
900.00	44.128	114.782	25.904
1000.00	46.084	119.530	30.417
1100.00	47.777	123.999	35.112
1200.00	49.245	128.217	39.965
1300.00	50.519	132.207	44.954
1400.00	51.627	135.989	50.063
1500.00	52.594	139.582	55.275
2000.00	55.915	155.209	82.489
2500.00	57.743	167.897	110.946
3000.00	58.832	178.526	140.111
3500.00	59.525	187.649	169.713
4000.00	59.990	195.628	199.599
4500.00	60.317	202.713	229.680
5000.00	60.554	209.080	259.901

Zero Point Vibration Energy (kcal/mol) = 52.5

(b) CH_2jSCH_2CHO

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	19.066	.008
50.00	10.556	51.416	.443
100.00	13.909	59.782	1.056
150.00	16.726	65.964	1.824
200.00	19.208	71.113	2.724
250.00	21.602	75.651	3.744
298.00	23.856	79.632	4.835
300.00	23.949	79.792	4.883
400.00	28.293	87.279	7.500
500.00	31.954	93.990	10.518
600.00	34.962	100.082	13.869
700.00	37.461	105.659	17.494
800.00	39.575	110.797	21.348
900.00	41.388	115.561	25.399
1000.00	42.955	120.001	29.618
1100.00	44.316	124.156	33.983
1200.00	45.499	128.061	38.475
1300.00	46.529	131.742	43.078
1400.00	47.428	135.222	47.777
1500.00	48.214	138.519	52.560
2000.00	50.931	152.795	77.416
2500.00	52.437	164.333	103.292
3000.00	53.337	173.977	129.754
3500.00	53.912	182.244	156.576
4000.00	54.298	189.469	183.635
4500.00	54.570	195.880	210.856
5000.00	54.767	201.640	238.193

Zero Point Vibration Energy (kcal/mol) = 43.7

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

Table B.1 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of CH_3SCH_2CHO and its Radicals. (Continued)

(c) $CH_3SCHjCHO$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	18.170	.008
50.00	9.938	50.274	.433
100.00	12.936	58.091	1.006
150.00	15.360	63.804	1.716
200.00	17.609	68.524	2.540
250.00	19.940	72.696	3.478
298.00	22.224	76.387	4.490
300.00	22.318	76.535	4.534
400.00	26.860	83.578	6.997
500.00	30.772	89.995	9.885
600.00	34.011	95.892	13.129
700.00	36.699	101.336	16.669
800.00	38.961	106.383	20.455
900.00	40.889	111.081	24.450
1000.00	42.546	115.473	28.624
1100.00	43.976	119.593	32.952
1200.00	45.213	123.470	37.413
1300.00	46.287	127.130	41.989
1400.00	47.220	130.593	46.665
1500.00	48.035	133.877	51.429
2000.00	50.833	148.114	76.219
2500.00	52.376	159.634	102.057
3000.00	53.296	169.269	128.493
3500.00	53.882	177.531	155.298
4000.00	54.276	184.752	182.344
4500.00	54.552	191.161	209.555
5000.00	54.753	196.919	236.884

Zero Point Vibration Energy (kcal/mol) = 45.0

(d) CH_3SCH_2CjO

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	18.279	.008
50.00	10.140	50.192	.429
100.00	13.920	58.472	1.038
150.00	16.306	64.584	1.796
200.00	18.478	69.565	2.665
250.00	20.742	73.924	3.645
298.00	22.947	77.749	4.694
300.00	23.038	77.903	4.740
400.00	27.372	85.125	7.265
500.00	31.090	91.635	10.193
600.00	34.185	97.577	13.462
700.00	36.780	103.041	17.014
800.00	38.987	108.094	20.805
900.00	40.884	112.794	24.801
1000.00	42.523	117.184	28.973
1100.00	43.945	121.301	33.298
1200.00	45.179	125.176	37.756
1300.00	46.252	128.833	42.329
1400.00	47.186	132.293	47.002
1500.00	48.002	135.575	51.762
2000.00	50.810	149.803	76.538
2500.00	52.361	161.320	102.367
3000.00	53.285	170.952	128.797
3500.00	53.874	179.212	155.597
4000.00	54.269	186.432	182.638
4500.00	54.547	192.841	209.846
5000.00	54.749	198.598	237.173

Zero Point Vibration Energy (kcal/mol) = 44.8

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

Table B.2 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of Radicals of CH_3CH_2SCHO and Its Radicals.

(a) CH_3CH_2SCHO				(b) CH_2jCH_2SCHO			
T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)	T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	18.375	.008	1.00	7.949	19.037	.008
50.00	9.866	50.592	.436	50.00	9.777	51.077	.431
100.00	12.779	58.298	1.000	100.00	12.940	58.796	.997
150.00	15.433	63.988	1.707	150.00	15.889	64.605	1.720
200.00	17.869	68.756	2.540	200.00	18.589	69.543	2.582
250.00	20.329	73.000	3.495	250.00	21.163	73.962	3.576
298.00	22.739	76.769	4.528	298.00	23.526	77.876	4.649
300.00	22.840	76.922	4.574	300.00	23.622	78.034	4.697
400.00	27.749	84.160	7.106	400.00	28.073	85.444	7.287
500.00	32.120	90.823	10.105	500.00	31.785	92.111	10.286
600.00	35.834	97.007	13.508	600.00	34.826	98.176	13.622
700.00	38.974	102.765	17.253	700.00	37.348	103.733	17.234
800.00	41.650	108.142	21.288	800.00	39.480	108.858	21.078
900.00	43.948	113.177	25.570	900.00	41.307	113.611	25.120
1000.00	45.931	117.908	30.067	1000.00	42.886	118.043	29.331
1100.00	47.646	122.363	34.748	1100.00	44.255	122.193	33.690
1200.00	49.132	126.571	39.588	1200.00	45.445	126.092	38.176
1300.00	50.421	130.552	44.567	1300.00	46.482	129.769	42.774
1400.00	51.542	134.328	49.667	1400.00	47.386	133.245	47.468
1500.00	52.519	137.915	54.871	1500.00	48.177	136.540	52.247
2000.00	55.872	153.525	82.057	2000.00	50.907	150.807	77.089
2500.00	57.716	166.205	110.497	2500.00	52.421	162.341	102.956
3000.00	58.813	176.830	139.651	3000.00	53.326	171.983	129.411
3500.00	59.511	185.951	169.244	3500.00	53.904	180.248	156.228
4000.00	59.980	193.928	199.124	4000.00	54.292	187.472	183.283
4500.00	60.308	201.012	229.201	4500.00	54.565	193.883	210.501
5000.00	60.547	207.379	259.418	5000.00	54.763	199.642	237.836
Zero Point Vibration Energy (kcal/mol) = 53.0				Zero Point Vibration Energy (kcal/mol) = 44.0			

Table B.2 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of Radicals of CH_3CH_2SCHO and Its Radicals. (Continued)

(c) $CH_3CHjSCHO$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	18.272	.008
50.00	10.991	50.930	.453
100.00	14.032	59.525	1.082
150.00	16.544	65.693	1.848
200.00	18.868	70.767	2.734
250.00	21.146	75.216	3.734
298.00	23.307	79.109	4.801
300.00	23.396	79.265	4.848
400.00	27.643	86.577	7.404
500.00	31.323	93.143	10.357
600.00	34.410	99.127	13.648
700.00	37.005	104.625	17.223
800.00	39.212	109.709	21.037
900.00	41.105	114.434	25.055
1000.00	42.737	118.847	29.249
1100.00	44.150	122.985	33.595
1200.00	45.373	126.877	38.072
1300.00	46.434	130.549	42.664
1400.00	47.357	134.022	47.355
1500.00	48.162	137.315	52.132
2000.00	50.923	151.584	76.975
2500.00	52.441	163.121	102.851
3000.00	53.344	172.767	129.316
3500.00	53.919	181.034	156.141
4000.00	54.305	188.260	183.203
4500.00	54.576	194.672	210.427
5000.00	54.772	200.432	237.767

Zero Point Vibration Energy (kcal/mol) = 44.1

(d) CH_3CH_2SCjO

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	18.317	.008
50.00	10.058	50.580	.438
100.00	12.980	58.430	1.013
150.00	15.743	64.219	1.732
200.00	18.218	69.086	2.582
250.00	20.530	73.396	3.552
298.00	22.670	77.179	4.589
300.00	22.758	77.331	4.634
400.00	26.952	84.451	7.123
500.00	30.635	90.862	10.007
600.00	33.762	96.724	13.231
700.00	36.412	102.126	16.744
800.00	38.675	107.134	20.501
900.00	40.621	111.799	24.468
1000.00	42.302	116.164	28.616
1100.00	43.757	120.262	32.921
1200.00	45.019	124.121	37.361
1300.00	46.115	127.766	41.919
1400.00	47.068	131.217	46.580
1500.00	47.899	134.491	51.329
2000.00	50.753	148.697	76.067
2500.00	52.325	160.203	101.872
3000.00	53.260	169.830	128.287
3500.00	53.856	178.087	155.077
4000.00	54.256	185.305	182.111
4500.00	54.536	191.712	209.313
5000.00	54.740	197.468	236.635

Zero Point Vibration Energy (kcal/mol) = 45.3

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

Table B3 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of Radicals of $CH_3SC(=O)CH_3$ and Its Radicals.

(a) $CH_3SC(=O)CH_3$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	16.035	.008
50.00	12.416	51.666	.524
100.00	14.779	61.021	1.206
150.00	16.971	67.420	2.000
200.00	19.242	72.605	2.905
250.00	21.602	77.145	3.926
298.00	23.916	81.130	5.018
300.00	24.012	81.290	5.066
400.00	28.702	88.837	7.705
500.00	32.864	95.689	10.788
600.00	36.399	101.993	14.256
700.00	39.395	107.828	18.050
800.00	41.958	113.253	22.121
900.00	44.169	118.320	26.430
1000.00	46.087	123.070	30.945
1100.00	47.753	127.539	35.639
1200.00	49.203	131.754	40.488
1300.00	50.466	135.740	45.473
1400.00	51.568	139.518	50.576
1500.00	52.531	143.107	55.782
2000.00	55.855	158.715	82.965
2500.00	57.695	171.391	111.394
3000.00	58.795	182.012	140.539
3500.00	59.495	191.130	170.123
4000.00	59.967	199.106	199.996
4500.00	60.298	206.188	230.067
5000.00	60.538	212.554	260.279

Zero Point Vibration Energy (kcal/mol) = 52.2

(b) $CH_2jSC(=O)CH_3$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	16.687	.008
50.00	10.441	49.595	.454
100.00	13.598	57.757	1.053
150.00	16.814	63.881	1.814
200.00	19.669	69.110	2.728
250.00	22.242	73.773	3.777
298.00	24.527	77.870	4.900
300.00	24.619	78.035	4.949
400.00	28.840	85.701	7.628
500.00	32.344	92.517	10.693
600.00	35.225	98.669	14.076
700.00	37.628	104.279	17.722
800.00	39.674	109.435	21.590
900.00	41.438	114.208	25.647
1000.00	42.971	118.651	29.870
1100.00	44.308	122.807	34.235
1200.00	45.475	126.711	38.726
1300.00	46.495	130.389	43.325
1400.00	47.387	133.866	48.020
1500.00	48.170	137.161	52.799
2000.00	50.886	151.423	77.632
2500.00	52.401	162.952	103.488
3000.00	53.309	172.590	129.934
3500.00	53.889	180.853	156.743
4000.00	54.280	188.075	183.792
4500.00	54.555	194.484	211.005
5000.00	54.755	200.243	238.335

Zero Point Vibration Energy (kcal/mol) = 43.6

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

Table B3 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of Radicals of $CH_3SC(=O)CH_3$ and Its Radicals. (Continued)

(c) $CH_3SC(=O)CH_2j$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	16.687	.008
50.00	10.555	49.366	.451
100.00	13.198	57.493	1.045
150.00	15.918	63.348	1.773
200.00	18.643	68.295	2.637
250.00	21.275	72.733	3.635
298.00	23.674	76.670	4.715
300.00	23.770	76.829	4.762
400.00	28.234	84.285	7.369
500.00	31.921	90.986	10.383
600.00	34.927	97.073	13.730
700.00	37.413	102.643	17.351
800.00	39.512	107.774	21.200
900.00	41.312	112.529	25.243
1000.00	42.870	116.960	29.454
1100.00	44.224	121.108	33.810
1200.00	45.404	125.005	38.293
1300.00	46.434	128.678	42.886
1400.00	47.335	132.150	47.576
1500.00	48.123	135.441	52.349
2000.00	50.859	149.694	77.165
2500.00	52.383	161.217	103.010
3000.00	53.296	170.853	129.447
3500.00	53.880	179.114	156.252
4000.00	54.273	186.335	183.296
4500.00	54.549	192.743	210.505
5000.00	54.750	198.501	237.833

Zero Point Vibration Energy (kcal/mol) = 44.1

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

Table B4 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of $CH_3SCH_2CH_3$ and Its Radicals.

(a) $CH_3SCH_2CH_3$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	14.689	.008
50.00	9.694	46.474	.423
100.00	12.863	54.194	.990
150.00	15.235	59.872	1.695
200.00	17.383	64.541	2.510
250.00	19.714	68.660	3.437
298.00	22.154	72.322	4.441
300.00	22.259	72.470	4.485
400.00	27.515	79.582	6.975
500.00	32.351	86.241	9.973
600.00	36.526	92.507	13.423
700.00	40.103	98.404	17.259
800.00	43.194	103.958	21.427
900.00	45.883	109.197	25.884
1000.00	48.231	114.150	30.593
1100.00	50.282	118.840	35.521
1200.00	52.074	123.289	40.640
1300.00	53.639	127.516	45.928
1400.00	55.008	131.539	51.362
1500.00	56.207	135.373	56.924
2000.00	60.357	152.162	86.172
2500.00	62.662	165.895	116.979
3000.00	64.040	177.448	148.681
3500.00	64.919	187.388	180.936
4000.00	65.510	196.096	213.553
4500.00	65.925	203.836	246.418
5000.00	66.228	210.798	279.460

Zero Point Vibration Energy (kcal/mol) = 64.0

(b) $CH_2jSCH_2CH_3$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	15.254	.008
50.00	9.286	46.843	.416
100.00	12.479	54.227	.959
150.00	15.362	59.845	1.657
200.00	17.864	64.604	2.489
250.00	20.312	68.847	3.443
298.00	22.687	72.610	4.475
300.00	22.785	72.762	4.520
400.00	27.562	79.969	7.041
500.00	31.751	86.571	10.013
600.00	35.281	92.672	13.369
700.00	38.273	98.334	17.051
800.00	40.850	103.610	21.010
900.00	43.095	108.548	25.210
1000.00	45.060	113.187	29.620
1100.00	46.783	117.560	34.214
1200.00	48.295	121.693	38.970
1300.00	49.620	125.609	43.867
1400.00	50.782	129.327	48.888
1500.00	51.802	132.863	54.018
2000.00	55.357	148.295	80.899
2500.00	57.345	160.876	109.119
3000.00	58.537	171.442	138.113
3500.00	59.300	180.525	167.586
4000.00	59.814	188.478	197.372
4500.00	60.175	195.544	227.374
5000.00	60.438	201.898	257.531

Zero Point Vibration Energy (kcal/mol) = 55.4

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

Table B4 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of $CH_3SCH_2CH_3$ and Its Radicals. (Continued)

(c) $CH_3SCHjCH_3$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	14.511	.008
50.00	9.905	46.337	.425
100.00	13.303	54.295	1.010
150.00	15.815	60.177	1.740
200.00	18.012	65.024	2.586
250.00	20.242	69.275	3.542
298.00	22.474	73.014	4.567
300.00	22.568	73.164	4.612
400.00	27.211	80.286	7.103
500.00	31.389	86.807	10.038
600.00	34.962	92.846	13.361
700.00	38.013	98.462	17.013
800.00	40.648	103.708	20.950
900.00	42.943	108.625	25.132
1000.00	44.950	113.250	29.529
1100.00	46.705	117.614	34.113
1200.00	48.241	121.742	38.862
1300.00	49.585	125.654	43.755
1400.00	50.761	129.369	48.774
1500.00	51.792	132.905	53.903
2000.00	55.369	148.338	80.785
2500.00	57.359	160.922	109.012
3000.00	58.551	171.491	138.013
3500.00	59.312	180.575	167.492
4000.00	59.823	188.530	197.284
4500.00	60.183	195.597	227.291
5000.00	60.445	201.951	257.451

Zero Point Vibration Energy (kcal/mol) = 55.4

(d) $CH_3SCH_2CH_2j$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	15.337	.008
50.00	9.711	47.089	.423
100.00	13.129	54.900	.997
150.00	15.753	60.731	1.721
200.00	18.134	65.583	2.568
250.00	20.562	69.882	3.535
298.00	22.944	73.690	4.579
300.00	23.043	73.844	4.625
400.00	27.829	81.127	7.173
500.00	32.000	87.787	10.170
600.00	35.500	93.931	13.550
700.00	38.458	99.624	17.252
800.00	41.005	104.923	21.228
900.00	43.223	109.878	25.442
1000.00	45.167	114.529	29.863
1100.00	46.873	118.912	34.467
1200.00	48.370	123.052	39.231
1300.00	49.684	126.973	44.135
1400.00	50.837	130.695	49.163
1500.00	51.850	134.235	54.298
2000.00	55.383	149.678	81.196
2500.00	57.360	162.263	109.426
3000.00	58.548	172.832	138.427
3500.00	59.308	181.916	167.904
4000.00	59.820	189.870	197.693
4500.00	60.179	196.936	227.698
5000.00	60.441	203.291	257.857

Zero Point Vibration Energy (kcal/mol) = 55. 1

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

Table B5 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of $HOOCH_2SCH_2CH_3$ and Its Radicals.

(a) $HOOCH_2SCH_2CH_3$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	20.351	.008
50.00	12.292	54.095	.486
100.00	17.212	64.167	1.228
150.00	20.794	71.853	2.183
200.00	23.756	78.237	3.297
250.00	26.766	83.850	4.559
298.00	29.806	88.801	5.917
300.00	29.934	89.000	5.976
400.00	36.260	98.471	9.289
500.00	41.883	107.169	13.204
600.00	46.598	115.222	17.635
700.00	50.537	122.700	22.498
800.00	53.873	129.663	27.723
900.00	56.733	136.170	33.257
1000.00	59.206	142.272	39.057
1100.00	61.354	148.013	45.087
1200.00	63.224	153.429	51.318
1300.00	64.856	158.551	57.724
1400.00	66.282	163.407	64.282
1500.00	67.531	168.020	70.974
2000.00	71.868	188.094	105.935
2500.00	74.290	204.409	142.529
3000.00	75.744	218.089	180.066
3500.00	76.674	229.837	218.187
4000.00	77.301	240.118	256.690
4500.00	77.742	249.248	295.457
5000.00	78.063	257.456	334.412

Zero Point Vibration Energy (kcal/mol) = 69.0

(b) $jOOCH_2SCH_2CH_3$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	20.265	.008
50.00	12.818	56.765	.535
100.00	16.390	66.759	1.266
150.00	19.327	73.972	2.162
200.00	22.010	79.892	3.195
250.00	24.844	85.096	4.366
298.00	27.733	89.697	5.627
300.00	27.855	89.882	5.683
400.00	33.866	98.712	8.772
500.00	39.191	106.844	12.432
600.00	43.641	114.384	16.580
700.00	47.347	121.388	21.135
800.00	50.470	127.912	26.030
900.00	53.135	134.007	31.214
1000.00	55.425	139.721	36.645
1100.00	57.402	145.093	42.289
1200.00	59.114	150.159	48.116
1300.00	60.599	154.947	54.104
1400.00	61.890	159.482	60.230
1500.00	63.016	163.789	66.476
2000.00	66.886	182.496	99.053
2500.00	69.018	197.666	133.078
3000.00	70.289	210.368	167.931
3500.00	71.098	221.266	203.292
4000.00	71.642	230.796	238.985
4500.00	72.023	239.257	274.906
5000.00	72.300	246.860	310.991

Zero Point Vibration Energy (kcal/mol) = 61.7

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

Table B5 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of $HOOCH_2SCH_2CH_3$ and Its Radicals. (Continued)

(c) $HOOCH_2SCHjCH_3$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	20.269	.008
50.00	13.397	54.539	.506
100.00	18.433	65.467	1.309
150.00	21.958	73.635	2.324
200.00	24.837	80.345	3.495
250.00	27.651	86.181	4.807
298.00	30.418	91.266	6.200
300.00	30.534	91.469	6.261
400.00	36.158	101.020	9.599
500.00	41.074	109.620	13.468
600.00	45.157	117.470	17.786
700.00	48.553	124.685	22.477
800.00	51.421	131.353	27.479
900.00	53.879	137.549	32.747
1000.00	56.004	143.333	38.244
1100.00	57.851	148.754	43.939
1200.00	59.460	153.855	49.806
1300.00	60.865	158.667	55.824
1400.00	62.094	163.220	61.973
1500.00	63.171	167.539	68.238
2000.00	66.918	186.271	100.855
2500.00	69.014	201.444	134.885
3000.00	70.275	214.144	169.733
3500.00	71.082	225.039	205.086
4000.00	71.626	234.567	240.771
4500.00	72.009	243.026	276.685
5000.00	72.288	250.627	312.763

Zero Point Vibration Energy (kcal/mol) = 60.1

(d) $HOOCH_2SCH_2CH_2j$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	20.860	.008
50.00	11.700	54.101	.471
100.00	16.150	63.577	1.168
150.00	20.145	70.889	2.078
200.00	23.723	77.172	3.175
250.00	27.125	82.824	4.447
298.00	30.287	87.851	5.825
300.00	30.416	88.054	5.886
400.00	36.453	97.637	9.237
500.00	41.483	106.317	13.142
600.00	45.553	114.243	17.501
700.00	48.888	121.515	22.229
800.00	51.686	128.223	27.261
900.00	54.080	134.446	32.552
1000.00	56.152	140.249	38.066
1100.00	57.957	145.682	43.774
1200.00	59.534	150.790	49.650
1300.00	60.914	155.608	55.674
1400.00	62.125	160.164	61.827
1500.00	63.189	164.485	68.094
2000.00	66.907	183.216	100.712
2500.00	68.999	198.386	134.735
3000.00	70.260	211.083	169.574
3500.00	71.069	221.977	204.921
4000.00	71.616	231.503	240.600
4500.00	72.000	239.961	276.510
5000.00	72.281	247.562	312.583

Zero Point Vibration Energy (kcal/mol) = 60.32

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

Table B6 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of $CH_3SCH(OOH)CH_3$ and Its Radicals.

(a) $CH_3SCH(OOH)CH_3$				(b) $CH_2jSCH(OOH)CH_3$			
T(K)	Cp	S	[H(T)-H(0K)]	T(K)	Cp	S	[H(T)-H(0K)]
	(cal/mol/K)	(cal/mol/K)	(kcal/mol)		(cal/mol/K)	(cal/mol/K)	(kcal/mol)
1.00	7.949	17.970	.008	1.00	7.949	18.642	.008
50.00	11.131	50.242	.443	50.00	10.629	50.804	.437
100.00	16.874	59.788	1.149	100.00	16.289	59.892	1.111
150.00	21.016	67.446	2.102	150.00	20.972	67.414	2.047
200.00	24.355	73.950	3.237	200.00	24.707	73.963	3.192
250.00	27.555	79.720	4.535	250.00	28.061	79.832	4.512
298.00	30.656	84.815	5.932	298.00	31.120	85.016	5.933
300.00	30.785	85.020	5.994	300.00	31.245	85.224	5.995
400.00	37.046	94.730	9.390	400.00	37.055	95.014	9.418
500.00	42.532	103.589	13.376	500.00	41.907	103.809	13.374
600.00	47.113	111.750	17.865	600.00	45.853	111.801	17.769
700.00	50.939	119.298	22.774	700.00	49.101	119.112	22.521
800.00	54.185	126.309	28.034	800.00	51.838	125.845	27.572
900.00	56.974	132.849	33.595	900.00	54.187	132.083	32.876
1000.00	59.392	138.974	39.417	1000.00	56.226	137.895	38.399
1100.00	61.498	144.730	45.463	1100.00	58.006	143.335	44.112
1200.00	63.336	150.157	51.707	1200.00	59.565	148.446	49.993
1300.00	64.943	155.287	58.123	1300.00	60.932	153.266	56.019
1400.00	66.350	160.149	64.689	1400.00	62.133	157.823	62.174
1500.00	67.585	164.766	71.387	1500.00	63.190	162.144	68.441
2000.00	71.885	184.850	106.364	2000.00	66.893	180.873	101.054
2500.00	74.295	201.167	142.963	2500.00	68.984	196.040	135.070
3000.00	75.745	214.848	180.502	3000.00	70.247	208.734	169.902
3500.00	76.674	226.596	218.622	3500.00	71.058	219.626	205.243
4000.00	77.300	236.876	257.125	4000.00	71.607	229.151	240.917
4500.00	77.741	246.007	295.892	4500.00	71.993	237.608	276.822
5000.00	78.062	254.214	334.847	5000.00	72.274	245.208	312.893
Zero Point Vibration Energy (kcal/mol) = 68.6				Zero Point Vibration Energy (kcal/mol) = 60.0			

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

Table B6 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of $CH_3SCH(OOH)CH_3$ and Its Radicals. (Continued)

(c) $CH_3SCH(OOj)CH_3$

T(K)	Cp	S	[H(T)-H(0K)]
	(cal/mol/K)	(cal/mol/K)	(kcal/mol)
1.00	7.949	17.865	.008
50.00	11.574	50.797	.462
100.00	16.163	60.279	1.160
150.00	19.698	67.520	2.060
200.00	22.717	73.598	3.122
250.00	25.678	78.976	4.331
298.00	28.572	83.725	5.633
300.00	28.693	83.916	5.691
400.00	34.575	92.972	8.858
500.00	39.746	101.245	12.581
600.00	44.068	108.875	16.779
700.00	47.674	115.938	21.371
800.00	50.721	122.500	26.295
900.00	53.328	128.622	31.500
1000.00	55.575	134.354	36.948
1100.00	57.519	139.739	42.605
1200.00	59.206	144.813	48.444
1300.00	60.672	149.608	54.439
1400.00	61.949	154.149	60.572
1500.00	63.064	158.459	66.824
2000.00	66.904	177.175	99.416
2500.00	69.027	192.348	133.447
3000.00	70.293	205.051	168.302
3500.00	71.100	215.949	203.665
4000.00	71.643	225.480	239.359
4500.00	72.024	233.940	275.281
5000.00	72.301	241.543	311.365

Zero Point Vibration Energy (kcal/mol) = 61.4

(d) $CH_3SCH(OOH)CH_2j$

T(K)	Cp	S	[H(T)-H(0K)]
	(cal/mol/K)	(cal/mol/K)	(kcal/mol)
1.00	7.949	18.690	.008
50.00	11.355	51.092	.447
100.00	17.256	60.851	1.169
150.00	21.548	68.690	2.144
200.00	25.076	75.372	3.312
250.00	28.372	81.315	4.648
298.00	31.426	86.553	6.084
300.00	31.551	86.763	6.147
400.00	37.365	96.642	9.600
500.00	42.199	105.505	13.587
600.00	46.111	113.547	18.009
700.00	49.324	120.895	22.786
800.00	52.029	127.656	27.857
900.00	54.351	133.916	33.179
1000.00	56.368	139.744	38.717
1100.00	58.130	145.196	44.444
1200.00	59.673	150.317	50.336
1300.00	61.028	155.145	56.372
1400.00	62.218	159.709	62.536
1500.00	63.266	164.035	68.811
2000.00	66.940	182.782	101.455
2500.00	69.016	197.958	135.490
3000.00	70.270	210.657	170.335
3500.00	71.075	221.552	205.686
4000.00	71.620	231.079	241.368
4500.00	72.003	239.537	277.279
5000.00	72.283	247.138	313.354

Zero Point Vibration Energy (kcal/mol) = 59.5

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

Table B7 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of $CH_3SCH_2CH_2OOH$ and Its Radicals.

(a) $CH_3SCH_2CH_2OOH$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	20.234	.008
50.00	11.267	52.717	.449
100.00	15.336	61.888	1.124
150.00	17.974	68.623	1.959
200.00	20.382	74.114	2.918
250.00	23.074	78.938	4.003
298.00	25.937	83.224	5.178
300.00	26.060	83.398	5.230
400.00	32.220	91.727	8.146
500.00	37.795	99.516	11.653
600.00	42.503	106.824	15.675
700.00	46.449	113.671	20.128
800.00	49.795	120.089	24.945
900.00	52.666	126.116	30.072
1000.00	55.149	131.790	35.465
1100.00	57.305	137.144	41.091
1200.00	59.182	142.208	46.917
1300.00	60.820	147.007	52.919
1400.00	62.251	151.564	59.074
1500.00	63.505	155.899	65.363
2000.00	67.860	174.818	98.316
2500.00	70.291	190.240	132.908
3000.00	71.751	203.191	168.448
3500.00	72.686	214.324	204.573
4000.00	73.316	224.072	241.083
4500.00	73.759	232.733	277.858
5000.00	74.082	240.521	314.822

Zero Point Vibration Energy (kcal/mol) = 68.8

(b) $CH_2jSCH_2CH_2OOH$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	20.854	.008
50.00	13.088	55.086	.501
100.00	18.259	65.842	1.293
150.00	21.830	73.950	2.300
200.00	24.752	80.628	3.465
250.00	27.636	86.452	4.775
298.00	30.470	91.539	6.169
300.00	30.589	91.743	6.230
400.00	36.304	101.324	9.579
500.00	41.239	109.959	13.464
600.00	45.299	117.838	17.798
700.00	48.653	125.072	22.500
800.00	51.479	131.751	27.511
900.00	53.899	137.951	32.783
1000.00	55.993	143.736	38.280
1100.00	57.818	149.155	43.972
1200.00	59.411	154.252	49.836
1300.00	60.805	159.060	55.848
1400.00	62.028	163.609	61.991
1500.00	63.101	167.923	68.248
2000.00	66.852	186.634	100.831
2500.00	68.961	201.794	134.831
3000.00	70.233	214.485	169.655
3500.00	71.049	225.375	204.989
4000.00	71.599	234.899	240.659
4500.00	71.987	243.355	276.561
5000.00	72.270	250.954	312.629

Zero Point Vibration Energy (kcal/mol) = 60.3

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

Table B7 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of $CH_3SCH_2CH_2OOH$ and Its Radicals. (Continued)

(c) $CH_3SCHjCH_2OOH$				(d) $CH_3SCH_2CH_2OOj$			
T(K)	Cp	S	[H(T)-H(0K)]	T(K)	Cp	S	[H(T)-H(0K)]
	(cal/mol/K)	(cal/mol/K)	(kcal/mol)		(cal/mol/K)	(cal/mol/K)	(kcal/mol)
1.00	7.949	20.249	.008	1.00	7.949	20.115	.008
50.00	12.802	54.454	.500	50.00	13.447	54.809	.515
100.00	17.555	64.875	1.266	100.00	17.364	65.452	1.295
150.00	20.938	72.651	2.232	150.00	19.895	72.986	2.229
200.00	23.935	79.079	3.354	200.00	22.250	79.021	3.282
250.00	26.950	84.735	4.626	250.00	24.888	84.257	4.459
298.00	29.890	89.711	5.990	298.00	27.674	88.855	5.720
300.00	30.013	89.911	6.050	300.00	27.793	89.041	5.775
400.00	35.870	99.347	9.349	400.00	33.732	97.840	8.854
500.00	40.899	107.896	13.195	500.00	39.057	105.941	12.500
600.00	45.031	115.719	17.499	600.00	43.524	113.458	16.636
700.00	48.444	122.916	22.178	700.00	47.247	120.445	21.180
800.00	51.316	129.571	27.169	800.00	50.385	126.957	26.066
900.00	53.772	135.754	32.427	900.00	53.062	133.043	31.242
1000.00	55.896	141.526	37.913	1000.00	55.363	138.750	36.666
1100.00	57.742	146.937	43.597	1100.00	57.348	144.116	42.304
1200.00	59.352	152.028	49.453	1200.00	59.067	149.177	48.127
1300.00	60.760	156.832	55.461	1300.00	60.557	153.962	54.109
1400.00	61.992	161.378	61.600	1400.00	61.853	158.495	60.232
1500.00	63.074	165.690	67.854	1500.00	62.983	162.799	66.475
2000.00	66.843	184.396	100.429	2000.00	66.866	181.498	99.039
2500.00	68.959	199.555	134.427	2500.00	69.005	196.665	133.056
3000.00	70.233	212.246	169.249	3000.00	70.280	209.365	167.902
3500.00	71.049	223.136	204.584	3500.00	71.091	220.261	203.259
4000.00	71.600	232.660	240.255	4000.00	71.636	229.791	238.949
4500.00	71.988	241.116	276.157	4500.00	72.019	238.251	274.868
5000.00	72.271	248.715	312.226	5000.00	72.297	245.853	310.951
Zero Point Vibration Energy (kcal/mol) = 60.7				Zero Point Vibration Energy (kcal/mol) = 61.8			

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

Table B8 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of CH_3SCH_2OH, $CH_3CH_2SCH_2OH$, $CH_3S(=O)CH_2OH$ and $CH_3S(=O)CH(OH)CH_3$.

(a) CH_3SCH_2OH

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	16.638	.008
50.00	8.554	47.875	.403
100.00	10.534	54.426	.882
150.00	12.052	58.990	1.448
200.00	13.549	62.654	2.087
250.00	15.295	65.856	2.807
298.00	17.182	68.696	3.586
300.00	17.264	68.811	3.620
400.00	21.368	74.331	5.553
500.00	25.110	79.501	7.881
600.00	28.292	84.360	10.556
700.00	30.981	88.922	13.523
800.00	33.282	93.207	16.739
900.00	35.272	97.240	20.169
1000.00	37.006	101.043	23.785
1100.00	38.522	104.639	27.563
1200.00	39.849	108.045	31.483
1300.00	41.013	111.279	35.527
1400.00	42.034	114.354	39.681
1500.00	42.931	117.283	43.930
2000.00	46.070	130.101	66.259
2500.00	47.837	140.584	89.776
3000.00	48.904	149.405	113.982
3500.00	49.588	156.996	138.616
4000.00	50.050	163.649	163.533
4500.00	50.375	169.563	188.644
5000.00	50.613	174.883	213.894

Zero Point Vibration Energy (kcal/mol) = 48.9

(b) $CH_3CH_2SCH_2OH$

T(K)	Cp (cal/mol/K)	S (cal/mol/K)	[H(T)-H(0K)] (kcal/mol)
1.00	7.949	18.751	.008
50.00	10.475	51.154	.443
100.00	13.953	59.486	1.055
150.00	17.010	65.729	1.831
200.00	19.808	71.000	2.752
250.00	22.658	75.716	3.813
298.00	25.509	79.930	4.969
300.00	25.629	80.101	5.020
400.00	31.553	88.277	7.882
500.00	36.860	95.890	11.309
600.00	41.348	103.007	15.226
700.00	45.126	109.663	19.555
800.00	48.345	115.896	24.232
900.00	51.119	121.747	29.209
1000.00	53.527	127.254	34.444
1100.00	55.626	132.451	39.904
1200.00	57.458	137.367	45.560
1300.00	59.059	142.026	51.388
1400.00	60.461	146.452	57.366
1500.00	61.691	150.663	63.474
2000.00	65.971	169.048	95.499
2500.00	68.368	184.044	129.137
3000.00	69.809	196.643	163.710
3500.00	70.731	207.476	198.861
4000.00	71.354	216.962	234.391
4500.00	71.792	225.392	270.184
5000.00	72.110	232.973	306.163

Zero Point Vibration Energy (kcal/mol) = 67.5

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

Table B8 Ideal Gas-Phase Thermodynamic Property vs. Temperature[a] of CH_3SCH_2OH, $CH_3CH_2SCH_2OH$, $CH_3S(=O)CH_2OH$ and $CH_3S(=O)CH(OH)CH_3$. (Continued)

(c) $CH_3S(=O)CH_2OH$				(d) $CH_3S(=O)CH(OH)CH_3$			
T(K)	Cp	S	[H(T)-H(0K)]	T(K)	Cp	S	[H(T)-H(0K)]
	(cal/mol/K)	(cal/mol/K)	(kcal/mol)		(cal/mol/K)	(cal/mol/K)	(kcal/mol)
1.00	7.949	18.405	.008	1.00	7.949	17.491	.008
50.00	9.385	49.967	.416	50.00	9.597	49.195	.421
100.00	13.294	57.638	.981	100.00	14.164	57.181	1.011
150.00	16.709	63.694	1.735	150.00	18.529	63.761	1.831
200.00	19.511	68.885	2.642	200.00	22.362	69.615	2.855
250.00	22.142	73.516	3.683	250.00	25.990	74.987	4.064
298.00	24.642	77.612	4.806	298.00	29.398	79.834	5.394
300.00	24.745	77.777	4.856	300.00	29.538	80.031	5.452
400.00	29.681	85.572	7.582	400.00	36.209	89.443	8.746
500.00	33.912	92.653	10.768	500.00	41.938	98.143	12.662
600.00	37.391	99.145	14.339	600.00	46.680	106.210	17.101
700.00	40.264	105.124	18.226	700.00	50.622	113.700	21.972
800.00	42.684	110.656	22.376	800.00	53.955	120.674	27.205
900.00	44.756	115.801	26.751	900.00	56.813	127.191	32.747
1000.00	46.550	120.607	31.318	1000.00	59.285	133.302	38.555
1100.00	48.112	125.114	36.053	1100.00	61.432	139.049	44.593
1200.00	49.476	129.357	40.934	1200.00	63.301	144.472	50.832
1300.00	50.671	133.362	45.943	1300.00	64.932	149.600	57.245
1400.00	51.718	137.154	51.064	1400.00	66.357	154.462	63.811
1500.00	52.639	140.752	56.282	1500.00	67.604	159.080	70.511
2000.00	55.857	156.374	83.487	2000.00	71.929	179.174	105.505
2500.00	57.670	169.046	111.909	2500.00	74.338	195.501	142.126
3000.00	58.764	179.662	141.039	3000.00	75.781	209.189	179.684
3500.00	59.467	188.775	170.609	3500.00	76.704	220.942	217.822
4000.00	59.941	196.748	200.468	4000.00	77.325	231.226	256.338
4500.00	60.276	203.827	230.527	4500.00	77.762	240.359	295.116
5000.00	60.519	210.191	260.729	5000.00	78.079	248.569	334.080
Zero Point Vibration Energy (kcal/mol) = 51.9				Zero Point Vibration Energy (kcal/mol) = 69.3			

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

REFERENCES

1) Molecular Weight: http://www.webqc.org/mmcalc.php.

2) http://www.lenntech.com/calculators/molecular/molecular-weight-calculator.htm (Accessed in 4/15/2011).

3) F. A. Carey, R. J. Sundberg, "Advance Organic Chemistry, Part A: Structure and Mechanisms, 4th ed.", Charlottesville, VA: Springer, **2004**.

4) M. Munowitz, "Principles of Chemistry, 1st ed.", QD133 M984, **2000**.

5) A. Gunturu, J. W. Bozzelli, R. Asatryan, *Thermochemistry, bond energies and internal rotor barriers of methyl sulfuric acid, methyl sulfuric acid ester and their radicals*, J. of Physical Organic Chemistry, **2010**, 9999 1-12.

6) Li Zhu and J. W. Bozzelli, *The multi-channel reaction of CH_3S+O_2: thermochemistry and kinetic barriers*, J. Mol. Struct.: THERMOCHEM, vol: 728(**2005**) 147-157.

7) Asatryan R., Bozzelli J.W., Simmie J.M. Thermochemistry of Methyl and Ethyl Nitro, R-NO2, and Nitrite, RONO, Organic Compounds, J. Phys. Chem. A, 112 (2008) 3172-3185.

8) A. G. Vandeputte, M-F Reyniers et al., *Theoretical study of the thermal decomposition of dimethyl disulfide*, J. Phys. Chem. A **2010**, 114, 10531-10549.

9) Frank Jensen, "Introduction to Computational Chemistry", New York: Wiley, c**1999**.

10) David C. Young, "Computational chemistry: a practical guide for applying techniques to real world problems", New York: Wiley, c**1999**.

11) X. Zheng, E. M. Fisher and F. C. Gouldin et al. *Pyrolysis and oxidation of ethyl methyl sulfide in a flow reactor"*, Combustion and Flame. vol: 158 (**2011**) 1049-1058.

12) X. Zheng, E. M. Fisher and F. C. Gouldin et al. *Experimental and computational Study of diethyl sulfide pyrolysis and mechanism*, Proceedings of the Combustion Institute, vol: 32 (**2009**) 469-476.

13) E. Frisch and Micheal J. Frisch, "Gaussian 03 Pocket Reference", Carnegie, PA: Gaussian Inc. March **2003**.

14) NIST Webbook: http://webbook.nist.gov/chemistry/.

15) Daan Frenkel and Berend Smit: "Understanding Molecular Simulation From Alrorithms to Applications, 2nd Edition", San Diego, CA: Elsevier, **2002**.

16) S. Snitsiriwat and Joseph W. Bozzelli, *The Thermochemistry and Bond Energies of Nitro-alkanes, -Alkenes, -Carbonyls and Corresponding Nitrites*, NJIT Master Thesis, Jan. **2009**.

17) F. Jin, J. Bozzelli, R. Asatryan, *Thermodynamic and Kinetic Analysis on the Activation Reaction of Dimethyl Sulfide Radical with Oxygen,* **2011**, *to be submitted.*

18) Sh. P. Pillai, *Structure and Thermochemistry of Disulfide-Oxygen Species*, NJIT Master Thesis, Jan. **2008**.

19) G. da Silva and J. W. Bozzelli, Enthalpies of Formation, Bond Dissociation Energies, and Molecular Structures of the n-Aldehydes (Acetaldehyde, Propanal, Butanal, Pentanal, Hexanal and Heptanal) and Their Radicals*, J. Phys. Chem.* A **2006**, Vol: 110. 13058-13067.

20) http://www.spaceref.com/news/viewpr.html?pid=10216 (Accessed in 05/02/2011).

21) Gary V. and Stephen D. "Environmental Chemistry, A Global Perspective, 2nd Ed", Oxford, UK: Oxford University Press, **2005** P362.

22) http://en.wikipedia.org/wiki/Enthalpy_of_atomization (Accessed in 05/08/2011).

23) http://en.wikipedia.org/wiki/Standard_enthalpy_of_formation (Accessed in 05/08/2011).

24) Chad Sheng, Ph D Thesis, Chemical Engineering, New Jersey Institute of Technology, **2002**.