## 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

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

by<br>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 $\mathrm{H}_{2} \mathrm{~S}$ involve $\mathrm{SO}_{2}$ 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 $\left(\Delta_{\mathrm{f}} \mathrm{H}^{0}, \mathrm{~S}^{0}\right.$ and $\left.\mathrm{Cp}(\mathrm{T})\right)$ of methyl ethyl sulfide $\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}\right)$, a widely used sulfuric hydrocarbon, and its main partial oxidation products in the atmosphere $\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \quad \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}\right.$ and $\left.\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}\right)$. 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 ( $\mathrm{S}^{0}$ and $\mathrm{Cp}(\mathrm{T})$ ) are determined with the help of the Hf values and the data of moments of inertia and frequencies from the CBS-QB3 output files.

by<br>Guanghui Song

A Thesis<br>Submitted to the Faculty of New Jersey Institute of Technology<br>in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering<br>Otto H. York Department of<br>Chemical, Biological and Pharmaceutical Engineering



## 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<br>Date<br>Distinguished Professor of Chemistry and Environmental Science, NJIT<br>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: <br> 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

Chapter Page
1 INTRODUCTION ..... 1
1.1 Introduction ..... 1
1.2 Objective ..... 3
2 STRUCTURES, THERMOCHEMISTRY, INTERNAL ROTOR POTENTIALS AND CARBON-HYDROGEN BOND ENERGIES IN SULFIDE ALDEHYDES AND KETONES AS PRODUCTS OF ATMOSPHERIC PARTIAL OXIDATION ..... 6
Overview ..... 6
2.1 Calculation Methods. ..... 6
2.2 Results and Discussion ..... 7
2.2.1 Structure ..... 7
2.2.2 Heats of Formation and Enthalpies of Reaction ..... 12
2.2.3 C—H Bond Energies ..... 19
2.2.4 Frequencies and Moment of Inertia ..... 21
2.2.5 Internal Rotational Potentials ..... 21
2.2.6 $\mathrm{S}^{\circ} 298$ and $\mathrm{Cp}^{\circ}(\mathrm{T})$ ..... 27
2.3 Summary ..... 28
3 STRUCTURES, THERMOCHEMISTRY, INTERNAL ROTOR POTENTIALS AND CARBON - HYDROGEN BOND ENERGIES IN METHYL ETHYL SULFIDE AND INTERMEDIATES OF RADICAL REACTIONS WITH O $\mathrm{O}_{2}$. ..... 29
Overview ..... 29
3.1 Calculation Methods ..... 29

## TABLE OF CONTENTS <br> (Continued)

Chapter Page
3.2 Results and Discussion ..... 30
3.2.1 Structure ..... 30
3.2.2 Heats of Formation and Enthalpies of Reaction. ..... 38
3.2.3 X-H (X=C, O) Bond Energies ..... 42
3.2.4 Frequencies and Moments of Inertia ..... 45
3.2.5 Internal Rotational Potentials ..... 45
3.2.6 $\mathrm{S}^{\circ} 298$ and $\mathrm{Cp}^{\circ}(\mathrm{T})$ ..... 58
3.3 Summary ..... 59
APPENDIX A FREQUENCIES AND MOMENTS OF INERTIA FROM CBS-QB3 OUTPUT FILES ..... 60
APPENDIX B IDEAL GAS-PHASE THERMODYNAMIC PROPERTY VS. TEMPERATURE DIRECTLY FROM SMCPS OUTPUT FILES ..... 65
REFERENCES ..... 82

## LIST OF TABLES

Table Page
2.1 Standard Enthalpies of Formation of Reference Species at 298.15K ..... 16
2.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation ( $\Delta \mathrm{H}^{\mathrm{o}} \mathrm{f} 298$ ) of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}, \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and Their Radicals ..... 17
2.3 C-H Bond Energies ..... 20
2.4 298K Entropy and Data of Heat Capacity vs. Temperature ..... 33
3.1 Standard Enthalpies of Formation of Reference Species at 298.15 K. ..... 39
3.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation ( $\Delta \mathrm{H}^{\mathrm{o}}{ }^{\mathrm{f} 298}$ ) of the Parents and the Radicals ..... 40
$3.3 \mathrm{C}-\mathrm{H}$ bond Energies of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ Calculated in $\mathrm{kcal} / \mathrm{mol}$ ..... 42
$3.4 \mathrm{X}-\mathrm{H}(\mathrm{X}=\mathrm{C}, \mathrm{O})$ Bond Energies of $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ Calculated in $\mathrm{kcal} / \mathrm{mol}$ ..... 44
3.5 298K Entropy and Data of Heat Capacity vs. Temperature ..... 58
A. 1 Frequencies and Moments of Inertia From CBS-QB3 Output Files of Stable $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and Their Radicals Formed After Losing One H Atom ..... 61
A. 2 Frequencies and Moments of Inertia From CBS-QB3 Output Files of Stable $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ and Their Radicals Formed After Losing One H Atom ..... 62
A. 3 Frequencies and Moments of Inertia From CBS-QB3 Output Files of Stable $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ ..... 64
B. 1 Ideal Gas-Phase Thermodynamic Property vs. Temperature of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ and Its Radicals ..... 66
B. 2 Ideal Gas-Phase Thermodynamic Property vs. Temperature of Radicals of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and its Radicals ..... 68
B. 3 Ideal Gas-Phase Thermodynamic Property vs. Temperature of Radicals of $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and Its Radicals ..... 70

## LIST OF TABLES <br> (Continued)

Table Page
B. 4 Ideal Gas-Phase Thermodynamic Property vs. Temperature of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ and Its Radicals. ..... 72
B. 5 Ideal Gas-phase Thermodynamic Property vs. Temperature of $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ and Its Radicals ..... 74
B. 6 Ideal Gas-Phase Thermodynamic Property vs. Temperature of $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and Its Radicals ..... 76
B. 7 Ideal Gas-Phase Thermodynamic Property vs. Temperature of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ and Its Radicals ..... 78
B. 8 Ideal Gas-Phase Thermodynamic Property vs. Temperature of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$, $\left.\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}, \mathrm{CH}_{3} \mathrm{~S}=\mathrm{O}\right) \mathrm{CH}_{2} \mathrm{OH}$ and $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ ..... 80

## LIST OF FIGURES

Figure Page
1.1 Sulfur cycle in the nature ..... 2
2.1 Optimized structures of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{SCHjCHO}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}$ at CBS-QB3 level. ..... 8
2.2 Optimized structures of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}, \mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}, \mathrm{CH}_{3} \mathrm{CHjSCHO}$ and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}$ at CBS-QB3 level. ..... 9
2.3 Optimized structures of $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$, and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}$ at CBS-QB3 level ..... 11
2.4 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ at UB3LY/3-21G level ..... 22
2.5 Potential energy barriers for internal rotations in $\mathrm{CH}_{2} \mathrm{JCH}_{2} \mathrm{CHO}$ at UB3LY/3-21G level ..... 22
2.6 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SCHjCHO}$ at UB3LY/3-21G level ..... 23
2.7 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{Cj}=\mathrm{O}$ at UB3LY/3-21G level ..... 23
2.8 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ at UB3LY/3-21G level ..... 24
2.9 Potential energy barriers for internal rotations in $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}$ at UB3LY/3-21G level ..... 24
2.10 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{CHjSCHO}$ at UB3LY/3-21G level ..... 24
2.11 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCj}=\mathrm{O}$ at UB3LY/3-21G level ..... 25
2.12 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ at UB3LY/3-21G level ..... 25
2.13 Potential energy barriers for internal rotations in $\mathrm{CH}_{2} \mathrm{SCC}(=\mathrm{O}) \mathrm{CH}_{3}$ at UB3LY/3-21G level ..... 26

## LIST OF FIGURES (Continued)

Figures Page
2.14 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}$ at UB3LY/3-21G level ..... 26
3.1 Optimized structures of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ at CBS-QB3 level ..... 31
3.2 Optimized structures of $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{jOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$, $\mathrm{HOOCH}_{2} \mathrm{SCHjCH}_{3}$ and $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ at CBS-QB3 level. ..... 33
3.3 Optimized structures of $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{j} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$, $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOj}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2 \mathrm{j}}$ at $\mathrm{CBS}-\mathrm{QB} 3$ level ..... 34
3.4 Optimized structures of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}, \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$, $\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{OOH}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOj}$ at CBS-QB3 level. ..... 35
3.5 Optimized structure of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$ at $\mathrm{CBS}-\mathrm{QB} 3$ level ..... 36
3.6 Optimized structure of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}$ at $\mathrm{CBS}-\mathrm{QB} 3$ level ..... 37
3.7 Optimized structure of $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ at $\mathrm{CBS}-\mathrm{QB} 3$ level ..... 37
3.8 Optimized structure of $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ at $\mathrm{CBS}-\mathrm{QB} 3$ level ..... 37
3.9 Potential energy barriers for internal rotations of the CS-CC bond in $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}$ at B3LYP/6-31G(d, p), B3LYP/6-31+G (2d, p) and CBS-QB3 leve. ..... 46
3.10 Potential energy barriers for internal rotations of the QCS-CC
$\left(\mathrm{HOOCH}_{2} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$ bonds in QCS-CC $\left(\mathrm{HOOCH}_{2} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$, jQCS- $\mathrm{CC}\left(\mathrm{jOOCH}_{2} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$, QCS- $\mathrm{CjC}\left(\mathrm{HOOCH}_{2} \mathrm{~S}-\mathrm{CHjCH}_{3}\right)$ and QCS-CCj $\left(\mathrm{HOOCH}_{2} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{j}\right)$ at B3LYP/6-31G(d) level ..... 48
3.11 Potential energy barriers for internal rotations of the $\mathrm{CS}-\mathrm{C}(\mathrm{Q}) \mathrm{C}\left(\mathrm{CH}_{3} \mathrm{~S}-\right.$ $\mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}$ ) bonds in $\mathrm{CS}-\mathrm{C}(\mathrm{Q}) \mathrm{C}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}\right), \mathrm{CjS}-\mathrm{C}(\mathrm{Q}) \mathrm{C}$ $\left(\mathrm{CH}_{2} \mathrm{~S}-\mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}\right), \mathrm{CS}-\mathrm{C}(\mathrm{Qj}) \mathrm{C}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}(\mathrm{OOj}) \mathrm{CH}_{3}\right)$ and $\mathrm{CS}-$ $\mathrm{C}(\mathrm{Q}) \mathrm{Cj}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{2} \mathrm{j}\right)$ at B3LYP/6-31G(d) level. ..... 49

## LIST OF FIGURES <br> (Continued)

## Figures

## Page

3.12 Potential energy barriers for internal rotations of the $\mathrm{CS}-\mathrm{CCQ}\left(\mathrm{CH}_{3} \mathrm{~S}-\right.$ $\left.\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}\right)$ bonds in $\mathrm{CS}-\mathrm{CCQ}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}\right), \mathrm{CjS}-\mathrm{CCQ}$ $\left(\mathrm{CH}_{2} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}\right)$, $\mathrm{CS}-\mathrm{CjCQ}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}\right)$ and $\mathrm{CS}-$ $\mathrm{CCQj}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOj}\right)$ at B3LYP/6-31G(d) level50
3.13 Potential energy barriers for internal rotations of the C--Q bonds in Q- CSCC ( $\mathrm{HOO}-\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ ), $\mathrm{jQ}-\mathrm{CSCC}\left(\mathrm{jOO}-\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}\right)$, Q- $\mathrm{CSCjC}\left(\mathrm{HOO}-\mathrm{CH}_{2} \mathrm{SCHjCH}_{3}\right)$ and $\mathrm{Q}-\mathrm{CSCCj}\left(\mathrm{HOO}-\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}\right)$ at B3LYP/6-31G(d) level. ..... 51
3.14 Potential energy barriers for internal rotations of the C--Q bonds in CSC(-- Q)C $\left(\mathrm{CH}_{3} \mathrm{SCH}(-\mathrm{OOH}) \mathrm{CH}_{3}\right), \mathrm{CjSC}(-\mathrm{Q}) \mathrm{C}\left(\mathrm{CH}_{2} \mathrm{SCH}(-\mathrm{OOH}) \mathrm{CH}_{3}\right)$, $\mathrm{CSC}(-\mathrm{Qj}) \mathrm{C}\left(\mathrm{CH}_{3} \mathrm{SCH}(-\mathrm{OOj}) \mathrm{CH}_{3}\right)$ and $\mathrm{CSC}(-\mathrm{Q}) \mathrm{Cj}\left(\mathrm{CH}_{3} \mathrm{SCH}(-\right.$ $\mathrm{OOH}) \mathrm{CH}_{2 \mathrm{j}}$ ) at B3LYP/6-31G(d) level ..... 52
3.15 Potential energy barriers for internal rotations of the C--Q bonds in CSCC-
$\mathrm{Q}\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}-\mathrm{OOH}\right), \mathrm{CjSCC}-\mathrm{Q}\left(\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2}-\mathrm{OOH}\right), \mathrm{CSCjC}-\mathrm{Q}$ $\left(\mathrm{CH}_{3} \mathrm{SCHjCH}_{2}-\mathrm{OOH}\right)$ and $\mathrm{CSCC}-\mathrm{Qj}\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}-\mathrm{OOj}\right)$ at B3LYP/6- 31G(d) level ..... 53
3.16 Potential energy barriers for internal rotations of the CO--OH bonds in HO-- $\mathrm{OCSCC}\left(\mathrm{HO}-\mathrm{OCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}\right)$, $\mathrm{HO}-\mathrm{OCSCjC}\left(\mathrm{HO}-\mathrm{OCH}_{2} \mathrm{SCHjCH}_{3}\right)$ and $\mathrm{HO}-\mathrm{OCSCCj}\left(\mathrm{HO}-\mathrm{OCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}\right)$ at B3LYP/6-31G(d) level ..... 54
3.17 Potential energy barriers for internal rotations of the CO--OH bonds in $\mathrm{CSC}(\mathrm{O}--\mathrm{OH}) \mathrm{C}\left(\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{O}-\mathrm{OH}) \mathrm{CH}_{3}\right), \mathrm{CjSC}(\mathrm{O}-\mathrm{OH}) \mathrm{C}\left(\mathrm{CH}_{2} \mathrm{SCH}(\mathrm{O}-\right.$ $\left.\mathrm{OH}) \mathrm{CH}_{3}\right)$ and $\mathrm{CSC}(\mathrm{O}-\mathrm{OH}) \mathrm{Cj}\left(\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{O}-\mathrm{OH}) \mathrm{CH}_{2} \mathrm{j}\right)$ at $\mathrm{B} 3 \mathrm{LYP} / 6-31 \mathrm{G}(\mathrm{d})$ level. ..... 55
3.18 Potential energy barriers for internal rotations of the $\mathrm{CO}--\mathrm{OH}$ bonds in $\mathrm{CSCCO}-\mathrm{OH}\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{O}-\mathrm{OH}\right), \mathrm{CjSCCO}-\mathrm{OH}\left(\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{O}-\right.$ $\mathrm{OH})$ and $\mathrm{CSCjCO}-\mathrm{OH}\left(\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{O}-\mathrm{OH}\right)$ at B3LYP/6-31G(d) level. ..... 56
3.19 Potential energy barriers for internal rotation of the $\mathrm{CS}(=\mathrm{O})-\mathrm{COH}$ bond in $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ at B3LYP/6-31G(2d,2p) level ..... 57
3.20 Potential energy barriers for internal rotation of the $\mathrm{CS}(=\mathrm{O}) \mathrm{C}--\mathrm{OH}$ bond in $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ at B3LYP/6-31G(2d,2p) level ..... 57

## LIST OF FIGURES

(Continued)
Figures Page
3.21 Potential energy barriers for internal rotation of the $\mathrm{CS}(=\mathrm{O})-\mathrm{C}(\mathrm{OH}) \mathrm{C}$ bond in $\mathrm{CH} 3 \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ at B3LYP/6-31G(2d,2p) level. ..... 57
3.22 Potential energy barriers for internal rotation of the $\mathrm{CS}(=\mathrm{O}) \mathrm{C}(--\mathrm{OH}) \mathrm{C}$ bond in $\mathrm{CH} 3 \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ at $\mathrm{B} 3 \mathrm{LYP} / 6-31 \mathrm{G}(2 \mathrm{~d}, 2 \mathrm{p})$ level ..... 57

## 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 $\left(\mathrm{SO}_{2}\right)$ 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].
atmosphere


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 $\mathrm{CO}_{2}$, 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 $\mathrm{H}_{2} \mathrm{SO}_{4}$ and SOx , or reacted to form solid sulfur, which is stored or land filled [17, 21].

Methyl Ethyl sulfide $\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}\right)$ 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 ( $\mathrm{T}=298 \mathrm{~K}$ and $\mathrm{P}=1 \mathrm{~atm})$. When released into the atmosphere, it mainly undergoes photochemical radical reaction with $\mathrm{O}_{2}$, 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 $\mathrm{SO}_{2}$. 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 $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$, and the proposed intermediates of partial oxidation are $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$, sometimes also $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}, \quad \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}$, $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ and $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$. These products and intermediates in the atmosphere are also probable intermediates of the combustion reaction of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$. As a result, the thermochemistry of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$, 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$31+G(2 d, p)$ calculation levels have been applied in Gaussian 98, and composite CBSQB3 level has been performed in Gaussian 03 [13]. The geometric structures, enthalpies
of formation, $\mathrm{H}-\mathrm{X}(\mathrm{X}=\mathrm{C}, \mathrm{O})$ bond energies, frequencies and moments of inertia, internal rotational potentials and the entropy and heat capacity values at 298 K and 1 atm 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: $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ with the radicals of $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{SCHjCHO}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{Cj}=\mathrm{O}$; $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ with the radicals of $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}, \mathrm{CH} 3 \mathrm{CHjSCHO}$ and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCj}=\mathrm{O}$; and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ with the radicals of $\mathrm{CH}_{2} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}$.

Then in Chapter 3, at first the targets to study are methyl ethyl sulfide $\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}\right)$ and its radicals after one H atom is abstracted from the different carbon atoms: $\mathrm{CH}_{2} \mathrm{j} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$. Then the targets are the proposed intermediates during reactions of oxygen molecule $\mathrm{O}_{2}$ with each of the three of methyl ethyl sulfide's carbon radicals. The main intermediates from the radical reactions with $\mathrm{O}_{2}$, 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: $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ (with the radicals of $\mathrm{jOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$, $\mathrm{HOOCH}_{2} \mathrm{SCHjCH}_{3}$ and $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ ), $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ (with the radicals of $\mathrm{CH}_{2} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}, \quad \mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOj}) \mathrm{CH}_{3}$ and $\left.\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2} \mathrm{j}\right)$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ (with the radicals of $\mathrm{CH}_{2} \mathrm{jSCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}, \mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{OOH}$ and $\left.\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOj}\right)$.

In Chapter 3 the stable molecules of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}, \quad \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}$, $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ and $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ have also been studied, as they're also some common intermediates of methyl ethyl sulfide's radical reaction with $\mathrm{O}_{2}$.

## 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 $\left(\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}(298), \mathrm{S}^{\mathrm{o}}\right.$ and $\left.\mathrm{Cp}(\mathrm{T})\right)$, 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 $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and their radicals are based on the Density Functional Theory (DFT) and composite ab initio levels using Gaussian 98. Computation levels include B3LYP/6$31 \mathrm{G}(\mathrm{d}, \mathrm{p})$ 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 $(298 \mathrm{~K})$ 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 $\Delta_{\mathrm{f}} \mathrm{H}^{\circ}(298)$, as this method has the highest accuracy. $\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}(298)$ data are reported for each species $[8,18,19]$.

The Entropy $\mathrm{S}^{\circ}(\mathrm{T}=298 \mathrm{~K})$ and $\mathrm{Cp}^{\circ}(\mathrm{T}, \mathrm{T}=298-1500 \mathrm{~K})$ were calculated using the "SMCPS" 24$]$ (Statistical Mechanics for Heat Capacity and Entropy $\mathbb{C p}$ and $\underline{S}$ ) 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 $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ molecule and its three radicals: $\mathrm{CjH}_{2} \mathrm{SCH}_{2} \mathrm{CH} * \mathrm{O}, \mathrm{CH}_{3} \mathrm{SCjHCH}^{*} \mathrm{O}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{Cj} * \mathrm{O}$ with the bond distances and the angles illustrated. The dihedral angles for C-S-C-C and $\mathrm{S}-\mathrm{C}-\mathrm{C}=\mathrm{O}$, are described directly below the Figure.


Figure 2.1 Optimized structures of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{SCHjCHO}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}$ at CBS-QB3 level (Bond distances in $\AA$; Bond Angles in ${ }^{\circ}$ ).

First, in the stable $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ molecule, all the $\mathrm{C}--\mathrm{H}$ bonds are about $1.1 \mathrm{~A}^{\circ}$, both bonds of $\mathrm{C}-\mathrm{SCC} * \mathrm{O}$ and $\mathrm{CS}-\mathrm{CC} * \mathrm{O}$ are about $1.8 \mathrm{~A}^{\circ}, \mathrm{CSC}-\mathrm{C} * \mathrm{O}$ is $1.51 \mathrm{~A}^{\circ}$ and $\operatorname{CSCC}(==) \mathrm{O}$ is $1.21 \mathrm{~A}^{\circ}$. And the $\mathrm{C}-\mathrm{S}-\mathrm{CC} * \mathrm{O}$ angle is $100.1^{\circ}$, the $\mathrm{CS}-\mathrm{C}-\mathrm{C}^{*} \mathrm{O}$ angle is $107.6^{\circ}$, the $\mathrm{CSC}-\mathrm{C}==\mathrm{O}$ angle is $123.7^{\circ}$. Then, for the radicals, when compared to the parent: 1) in $\mathrm{CH}_{2} \mathrm{jSCH}_{2} \mathrm{CHO}, \mathrm{C}-\mathrm{SCC} * \mathrm{O}$ has shortened evidently to $1.72 \mathrm{~A}^{\circ}$; 2)in $\mathrm{CH}_{3} \mathrm{SCHjCHO}, \mathrm{C}-\mathrm{S}-\mathrm{CC} * \mathrm{O}$ has increased to $106.7^{\circ}, \mathrm{CS}-\mathrm{C}-\mathrm{C} * \mathrm{O}$ has increased to
$129.5^{\circ}$, and $\mathrm{CS}-\mathrm{CC} * \mathrm{O}$ has shortened evidently to $1.71 \mathrm{~A}^{\circ}, \mathrm{CSC}-\mathrm{C}^{*} \mathrm{O}$ has decreased to $1.43 \mathrm{~A}^{\circ}$; 3)in $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}, \mathrm{CS}-\mathrm{C}-\mathrm{C}^{*} \mathrm{O}$ has increased evidently to $117.7^{\circ}$ and $\mathrm{CSC}-$ $\mathrm{C}==\mathrm{O}$ has increased to $130.7^{\circ}$, but there is no evident change to each bond compared to the parent molecule.

(a) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$
$\mathrm{C}-\mathrm{C}-\mathrm{S}-\mathrm{C}=-84.3^{\circ} \mathrm{C}-\mathrm{S}-\mathrm{C}=\mathrm{O}=-0.5^{\circ}$

(b) $\mathrm{CH}_{2} \mathrm{jCH} 2 \mathrm{SCHO} \quad \mathrm{C}-\mathrm{C}-\mathrm{S}-\mathrm{C}=-81.5^{\circ}$
$\mathrm{C}-\mathrm{S}-\mathrm{C}=\mathrm{O}=-0.6^{\circ}$


(d) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCj} * \mathrm{O} \quad \mathrm{C}-\mathrm{C}-\mathrm{S}-\mathrm{C}=77.3^{\circ} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}=\mathrm{O}=0.1^{\circ}$

Figure 2.2 Optimized structures of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}, \mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}, \mathrm{CH}_{3} \mathrm{CHjSCHO}$ and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}$ at CBS-QB3 level (Bond distances in $\AA$; Bond Angles in ${ }^{\circ}$ ).

Figure 2.2 shows the four lowest energy configurations of the stable $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ molecule and its three radicals $\mathrm{CjH}_{2} \mathrm{CH}_{2} \mathrm{SCH}^{*} \mathrm{O} \mathrm{CH}_{3} \mathrm{CjHSCH}^{*} \mathrm{O}$, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCj}^{*} \mathrm{O}$ 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 $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ molecule has all $\mathrm{C}--\mathrm{H}$ bond lengths also about $1.1 \mathrm{~A}^{\circ}$, $\mathrm{C}-\mathrm{CSC} * \mathrm{O}$ is $1.53 \mathrm{~A}^{\circ}, \mathrm{CC}-\mathrm{SC} * \mathrm{O}$ is $1.83 \mathrm{~A}^{\circ}, \mathrm{CCS}-\mathrm{C} * \mathrm{O}$ is $1.78 \mathrm{~A}^{\circ}$ and $\mathrm{CCSC}==\mathrm{O}$ is $1.20 \mathrm{~A}^{\circ}$. And the angle of $\mathrm{C}-\mathrm{C}-\mathrm{SC} * \mathrm{O}$ is $113.5^{\circ}$, $\mathrm{CC}-\mathrm{S}--\mathrm{C}^{*} \mathrm{O}$ is $99.9^{\circ}$ and $\mathrm{CCS}-$ $\mathrm{C}==\mathrm{O}$ is $125.8^{\circ}$. Then, for the radicals, when compared to the parent: 1) in $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}, \mathrm{CC}-\mathrm{SC} * \mathrm{O}$ has increased evidently to $1.89 \mathrm{~A}^{\circ}, \mathrm{C}-\mathrm{C}-\mathrm{SC} * \mathrm{O}$ has decreased to $112.0^{\circ} ; 2$ ) in $\mathrm{CH}_{3} \mathrm{CHjSCHO}, \mathrm{CC}-\mathrm{SC}^{*} \mathrm{O}$ has shortened to $1.72 \mathrm{~A}^{\circ}, \mathrm{C}-\mathrm{C}-$ $\mathrm{SC} * \mathrm{O}$ has increased to $121.0^{\circ}$ and $\mathrm{CC}-\mathrm{S}-\mathrm{C} * \mathrm{O}$ has increased to $101.9^{\circ}$; 3) in $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}, \mathrm{CC}--\mathrm{SC} * \mathrm{O}$ has increased to $1.85 \mathrm{~A}^{\circ}, \mathrm{CC}-\mathrm{S}-\mathrm{C} * \mathrm{O}$ has increased to $102.7^{\circ}$ and $\mathrm{CCS}-\mathrm{C}==\mathrm{O}$ has increased to $130.2^{\circ}$.

(a) $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$
$\mathrm{C}-\mathrm{S}-\mathrm{C}=\mathrm{O}=0.0^{\circ}$
(b) $\mathrm{CH}_{2} \mathrm{JSC}(=\mathrm{O}) \mathrm{CH}_{3} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}=\mathrm{O}=0.0^{\circ}$

C-S-C-C $=180.0^{\circ}$
C-S-C-C $=-180.0^{\circ}$

(c) $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}=\mathrm{O}=0^{\circ} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{C}=180.0^{\circ}$

Figure 2.3 Optimized structures of $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{JCC}(=\mathrm{O}) \mathrm{CH}_{3}$, and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}$ at CBS-QB3 level (Bond distances in $\AA$; Bond Angles in ${ }^{\circ}$ ).

Figure 2.3 shows the three lowest energy configurations of the stable $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ molecule and its two radicals with bond distances and angles. The dihedral angles are listed directly below each figure.

In the stable $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$, all the $\mathrm{C}-\mathrm{H}$ bonds of are still about $1.1 \mathrm{~A}^{\circ}$, both $\mathrm{C}-\mathrm{SC}(* \mathrm{O}) \mathrm{C}$ and $\mathrm{CS}-\mathrm{C}(* \mathrm{O}) \mathrm{C}$ are also about $1.8 \mathrm{~A}^{\circ}, \mathrm{CSC}(==\mathrm{O}) \mathrm{C}$ is also about $1.2 \mathrm{~A}^{\circ}$, $\mathrm{CSC}(* \mathrm{O})-\mathrm{C}$ is $1.51 \mathrm{~A}^{\circ}$. And the angle of $\mathrm{C}-\mathrm{S}-\mathrm{C}(* \mathrm{O}) \mathrm{C}$ is $99.1^{\circ}, \mathrm{CS}-\mathrm{C}(==\mathrm{O}) \mathrm{C}$ is $122.4^{\circ}$ and $\mathrm{CSC}(==\mathrm{O})-\mathrm{C}$ is $123.8^{\circ}$. Then, for the radicals: 1$)$ in $\mathrm{CH}_{2} \mathrm{j} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}, \mathrm{C}-$ $\mathrm{SC}(* \mathrm{O}) \mathrm{C}$ has shortened to $1.71 \mathrm{~A}^{\circ}$, and $\mathrm{C}-\mathrm{S}-\mathrm{C}(* \mathrm{O}) \mathrm{C}$ has increased to $101.3^{\circ} ; 2$ ) in $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}, \mathrm{CSC}(==\mathrm{O})-\mathrm{C}$ has decreased to $1.44 \mathrm{~A}^{\circ}$, but there is no evident change in each bond angle.

After a hydrogen atom $(\mathrm{H})$ 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 $\mathrm{C}-\mathrm{S}$ bonds and $\mathrm{C}-\mathrm{H}$ 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 $\operatorname{CSC}(-\mathrm{H}) \mathrm{C} * \mathrm{O}$ and $\mathrm{H}-\mathrm{CSC}(* \mathrm{O}) \mathrm{C}$, leads to formation of a partial double bond ( $\pi$ bond) between the sulfur atom and the carbon atom: $\mathrm{CS}-. \mathrm{CC}=\mathrm{O}$ and $\mathrm{C}-. \mathrm{SC}(=\mathrm{O}) \mathrm{C}$. This also effects the double bond between the oxygen and carbon atom in the carbonyl group $\mathrm{C}(=\mathrm{O})$, 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 $\mathrm{T}=298 \mathrm{~K}\left(\Delta H^{o}{ }_{f 298}\right)$ :
i) Enthalpy of Atomization [22]. It's mainly used on gaseous molecules. Each work reaction follows the atom balance rule, using $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ as an example:

$$
\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}=3 \mathrm{C}+6 \mathrm{H}+\mathrm{S}+\mathrm{O}
$$

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 $\mathrm{T}=298.15 \mathrm{~K}$ and $\mathrm{P}=1 \mathrm{~atm}$ [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 ( $\mathrm{T}=298.15 \mathrm{~K}$ and $\mathrm{P}=1 \mathrm{~atm}$ ) [23]. Also, use a work reaction for $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ as an example:

$$
\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}=3 \mathrm{C}(\mathrm{~s})+3 \mathrm{H}_{2}+\mathrm{S}(\mathrm{~s})+1 / 2 \mathrm{O}_{2}
$$

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:

$$
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \\
& \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{4} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CHO}
\end{aligned}
$$

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:

$$
\begin{array}{ccccc}
\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{4} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CHO} \\
\text { Unknown } & -17.8 & -9.0 & -40.9 \quad \Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{o}} 298 \mathrm{kcal} \mathrm{~mol}^{-1}
\end{array}
$$

(Reference Species values from Literature)
$\Delta H^{\circ} \mathrm{rxn}, 298=\Delta H_{\mathrm{f}}{ }^{\circ} 298\left[\mathrm{CH}_{3} \mathrm{SCH}_{3}\right]+\Delta H_{\mathrm{f}}{ }^{\circ} 298\left[\mathrm{CH}_{3} \mathrm{CHO}\right]$

$$
\begin{aligned}
& \quad-\Delta H_{\mathrm{f}}{ }^{\circ}{ }_{298}\left[\mathrm{CH}_{4}\right]-\Delta H_{\mathrm{f}}{ }^{\circ}{ }_{298}\left[\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}\right] \\
& \Delta H^{\circ} \mathrm{rxn}, 298\left[\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}\right]=3.6 \mathrm{kcal} \mathrm{~mol}^{-1}(\text { This calculation }) \\
& \text { (This is calculated with DFT method) } \\
& \text { using } \Delta \mathrm{Hrxn}=\Sigma \Delta_{\mathrm{f}} \mathrm{H}^{\circ}(298) \text { products }-\Sigma \Delta_{\mathrm{f}} \mathrm{H}^{\circ}(298) \text { reactants } \\
& \quad 3.6=-9.0+(-40.9)-(-17.8)-\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}\right) \mathrm{kcal} \mathrm{~mol}{ }^{-1} \\
& \text { Find } \Delta H_{\mathrm{f}}{ }^{\circ}{ }_{298} \text { of } \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}=-35.6 \mathrm{kcal} / \mathrm{mol}
\end{aligned}
$$

In order to improve precision, several different work reactions were applied for each targeted species, this provides statistics and validation for the $\Delta_{f} \mathrm{H}^{0}(298)$ 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 $\Delta_{\mathrm{f}} \mathrm{H}^{\circ}(298)$ of the target parent and radical intermediates have been determined using calculated $\Delta_{f} H^{\circ}(298)$ values for each species, then calculating the $\Delta$ Hreaction at 298 K , and then using the known literature values for the three reference molecules in the work reaction and the calculated $\Delta \mathrm{Hrxn}$ find $\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}(298)$ of the target. The standard enthalpies of formation of the reference species at 298 K 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.
$\Delta \mathrm{H}_{\mathrm{rxn}(298)}=\sum \mathrm{H}_{\mathrm{f}}$ products $-\sum \mathrm{H}_{\mathrm{f}}$ reactants

The work reactions in Table 2.2 are used to calculate the heat of reaction and enthalpies of formation for $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}, \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ 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 $\Delta_{\mathrm{f}} \mathrm{H}^{\circ}(298)$, as this method has the highest accuracy. $\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}(298)$ 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 $\mathrm{C}-\mathrm{H}$ 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 | $\Delta \mathbf{H}_{\mathrm{f}}{ }^{\circ} 298($ kcal mol |  |
| :--- | :--- | :--- |
| $\left.\mathrm{CH}_{4}\right)$ | References |  |
| $\mathrm{CH}_{3} \mathrm{CH}_{3}$ | -17.83 | $[14]$ |
| $\mathrm{CH}_{3} \mathrm{SCH}_{3}$ | -20.04 | $[14]$ |
| $\mathrm{CH}_{3} \mathrm{CHO}$ | -40.96 | $[11]$ |
| $\mathrm{CH}_{3} \mathrm{OH}$ | -48.02 | $[14]$ |
| $\mathrm{CH}_{3} \mathrm{C}(=\mathrm{O}) \mathrm{OH}$ | -103.5 | $[14]$ |
| $\mathrm{CH}_{3} \mathrm{OCH}$ | -43.99 | $[14]$ |
| $\mathrm{CH}_{3} \mathrm{C}(=\mathrm{O}) \mathrm{OCH}_{3}$ | -98 | $[16]$ |
| $\mathrm{CH}_{3} \mathrm{C}(=\mathrm{O}) \mathrm{CH}_{3}$ | -51.56 | $[17]$ |
| $\mathrm{CH}_{3} \mathrm{SH}$ | -5.47 | $[16]$ |
| $\mathrm{CH}_{2} \mathrm{SH}$ | 37.7 | $[16]$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3}$ | -24.82 | $[14]$ |
| $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}$ | 23.67 | $[16]$ |
| $\mathrm{CH}_{2} \mathrm{CH}_{3}$ | 28.4 | $[12]$ |
| $\mathrm{CH}_{2} \mathrm{SCH}$ | 32.66 | $[12]$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ | -56.23 | $[14]$ |
| $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | -7.2 | $[19]$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ | -45.18 | $[19]$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Cj}=\mathrm{O}$ | -7.45 | $[19]$ |
| $\mathrm{CH}_{3} \mathrm{CHjCHO}^{2}$ | -7.1 | $[19]$ |
| $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CHO}$ | 5.1 | $[19]$ |
| $\mathrm{CH}_{2} \mathrm{CHO}$ | 3.6 | $[19]$ |
| $\mathrm{CH}_{3} \mathrm{Cj}=\mathrm{O}$ | -3 | $[19]$ |

Table 2.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation ( $\Delta \mathrm{H}^{\mathrm{o}}{ }_{\mathrm{f} 298}$ ) of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}, \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and Their Radicals (Units: $\mathrm{kcal} / \mathrm{mol})$.

| $\Delta \mathrm{H}_{\mathrm{f}}{ }_{298}\left(\mathrm{kcal} \mathrm{mol}{ }^{-1}\right)$ | B3LYP |  | $\begin{aligned} & \text { CBS- } \\ & \text { QB3 } \end{aligned}$ | Average |
| :---: | :---: | :---: | :---: | :---: |
| Work Reactions | 6-31G(d,p) | 6-31+G(2d,p) |  |  |
| $\mathbf{C H}_{3} \mathbf{S C H}_{2} \mathbf{C H O}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ | -35.1 | -35.0 | -35.6 | -35.3 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{4} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CHO}$ | -33.9 | -33.8 | -35.6 | -34.4 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{OH} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CO} 2 \mathrm{H}$ | -31.2 | -33.9 | -34.9 | -33.4 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{OCH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3}{\mathrm{CO} 22 \mathrm{CH}_{3}}$ | -32.1 | -33.9 | -34.2 | -33.4 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{C}(=\mathrm{O}) \mathrm{CH}_{3}$ | -33.7 | -33.6 | -34.2 | -33.8 |
| Average | -33.2 | -34.1 | -34.9 | -34.1 |
| $\mathbf{H f}=\mathbf{- 3 4 . 9}$, use the average value of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{2} \mathbf{j} \mathrm{SCH}_{2} \mathrm{CHO}$ |  |  |  |  |
| $\mathrm{CH}_{2} \mathrm{j} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{SH} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{2} \mathrm{j} \mathrm{SH}$ | 8.9 | 9.1 | 9.8 | 9.3 |
| $\mathrm{CH}_{2} \mathrm{jSCH} 2 \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}$ | 8.9 | 8.4 | 7.7 | 8.3 |
| $\mathrm{CH}_{2} \mathrm{jCCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{2} \mathrm{jCH}_{3}$ | 9.1 | 8.5 | 8.3 | 8.6 |
| $\mathrm{CH}_{2} \mathrm{j} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{SCH} 3 \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{2} \mathrm{SCH}_{3}$ | 8.6 | 9.1 | 8.9 | 8.9 |
| $\mathrm{CH}_{2} \mathrm{jSCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{OH}$ | 8.1 | 7.7 | 7.4 | 7.7 |
| Average | 8.7 | 8.6 | 8.4 | 8.6 |
| $\mathrm{Hf}=8.4$, use the average value of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCHjCHO}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCHjCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CjO}$ | -4.1 | -3.8 | -2.6 | -3.5 |
| $\mathrm{CH}_{3} \mathrm{SCHjCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CHjCHO}$ | -3.2 | -3.3 | -3.2 | -3.2 |
| $\mathrm{CH}_{3} \mathrm{SCHjCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CHO}$ | -5.6 | -5.3 | -2.6 | -4.5 |
| $\mathrm{CH}_{3} \mathrm{SCHjCHO}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{2} \mathrm{j} \mathrm{CHO}$ | -4.8 | -4.9 | -3.4 | -4.4 |
| $\mathrm{CH}_{3} \mathrm{SCHjCHO}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CjO}$ | -6.3 | -5.7 | -4.5 | -5.5 |
| Average | -4.8 | -4.6 | -3.3 | -4.2 |
| $\mathbf{H f}=\mathbf{- 3 . 3}$, use the average value of the CBS-QB3 level |  |  |  |  |
| $\mathbf{C H}_{3} \mathbf{S C H}_{2} \mathbf{C j O}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CjO}$ | 4.8 | 5.5 | 5.4 | 5.2 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CHjCHO}$ | 5.7 | 6.0 | 4.8 | 5.5 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CHO}$ | 3.3 | 4.0 | 5.5 | 4.3 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{2} \mathrm{j} \mathrm{CHO}$ | 4.1 | 4.4 | 4.6 | 4.4 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}+\mathrm{CH}_{3} \mathrm{CjO}$ | 2.6 | 3.6 | 3.5 | 3.3 |
| Average | 4.1 | 4.7 | 4.8 | 4.5 |
| $\mathrm{Hf}=4.8$, use the average value of the CBS-QB3 level |  |  |  |  |
| $\mathbf{C H}_{3} \mathbf{C H}_{2} \mathbf{S C H O}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ | -44.5 | -44.1 | -43.7 | -44.1 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{4} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CHO}$ | -43.3 | -42.9 | -43.7 | -43.3 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{OH} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CO} 2 \mathrm{H}$ | -40.6 | -43.0 | -43.0 | -42.2 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{OCH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CO} 2 \mathrm{CH}_{3}$ | -41.5 | -43.0 | -42.3 | -42.2 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{C}(=\mathrm{O}) \mathrm{CH}_{3}$ | -43.1 | -42.7 | -42.3 | -42.7 |
| Average | -42.6 | -43.2 | -43.0 | -42.9 |
| $\mathrm{Hf}=-43.0$, use the average value of the CBS-QB3 level |  |  |  |  |
| $\mathbf{C H}_{2} \mathbf{j C H}_{2} \mathbf{S C H O}$ |  |  |  |  |
| $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{SH} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{2} \mathrm{j} \mathrm{SH}$ | 4.2 | 5.0 | 6.9 | 5.4 |
| $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}$ | 4.1 | 4.3 | 4.7 | 4.4 |
| $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{2} \mathrm{jCH}_{3}$ | 4.3 | 4.4 | 5.3 | 4.7 |
| $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{SCH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{2} \mathrm{SCH}_{3}$ | 3.9 | 5.0 | 5.9 | 4.9 |
| $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{OH}$ | 3.3 | 3.6 | 4.4 | 3.8 |
| Average | 3.9 | 4.5 | 5.4 | 4.6 |
| $\mathrm{Hf}=5.4$, use the average value of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathbf{C H j S C H O}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{CHjSCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CjO}$ | 2.5 | 1.4 | 1.5 | 1.8 |
| $\mathrm{CH}_{3} \mathrm{CHjSCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CHjCHO}$ | 3.4 | 2.0 | 1.0 | 2.1 |
| $\mathrm{CH}_{3} \mathrm{CHjSCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CHO}$ | 1.0 | 0.0 | 1.6 | 0.9 |
| $\mathrm{CH}_{3} \mathrm{CHjSCHO}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{2} \mathrm{CHHO}$ | 1.8 | 0.4 | 0.7 | 1.0 |
| $\mathrm{CH}_{3} \mathrm{CHjSCHO}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CjO}$ | 0.3 | -0.4 | -0.3 | -0.2 |
| Average | 1.8 | 0.7 | 0.9 | 1.1 |
| $\mathrm{Hf}=0.9$, use the average value of the CBS-QB3 level |  |  |  |  |

Table 2.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation ( $\Delta \mathrm{H}^{\mathrm{o}}{ }^{\mathrm{f} 298}$ ) of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}, \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and Their Radicals (Units: $\mathrm{kcal} / \mathrm{mol}$ ).
(Continued)

| $\Delta \mathbf{H}_{\text {f }}{ }^{\text {o }}$ ( ${ }^{\text {(kcal mol }}{ }^{-1}$ ) | B3LYP |  | $\begin{aligned} & \text { CBS- } \\ & \text { QB3 } \\ & \hline \end{aligned}$ | Average |
| :---: | :---: | :---: | :---: | :---: |
| Work Reactions | 6-31G(d,p) | 6-31+G(2d,p) |  |  |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathbf{S C j O}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CjO}$ | -4.1 | -4.4 | -4.4 | -4.3 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CHjCHO}$ | -3.2 | -3.9 | -5.0 | -4.0 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CHO}$ | -5.6 | -5.8 | -4.4 | -5.3 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{2} \mathrm{j} \mathrm{CHO}$ | -4.8 | -5.4 | -5.3 | -5.2 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}+\mathrm{CH}_{3} \mathrm{CjO}$ | -6.3 | -6.2 | -6.3 | -6.3 |
| Average | -4.8 | -5.1 | -5.1 | -5.0 |
| $\mathbf{H f}=-5.1$, use the average value of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ | -51.1 | -50.8 | -50.8 | -50.9 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{4} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CHO}$ | -49.8 | -49.5 | -50.8 | -50.0 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{OH} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CO} 2 \mathrm{H}$ | -47.2 | -49.6 | -50.1 | -49.0 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{OCH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CO} 2^{2} \mathrm{CH}_{3}$ | -48.1 | -49.6 | -49.4 | -49.0 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{C}(=\mathrm{O}) \mathrm{CH}_{3}$ | -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 |  |  |  |  |
| $\mathrm{CH}_{2} \mathbf{j S C}(=0) \mathrm{CH}_{3}$ |  |  |  |  |
| $\mathrm{CH}_{2} \mathrm{SCC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SH} \rightarrow \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{SH}$ | -6.3 | -6.0 | -4.3 | -5.5 |
| $\mathrm{CH}_{2} \mathrm{jSC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}$ | -6.3 | -6.8 | -6.4 | -6.5 |
| $\mathrm{CH}_{2} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{CH}_{3}$ | -6.2 | -6.7 | -5.8 | -6.2 |
| $\mathrm{CH}_{2} \mathrm{j} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{SCH}_{3}$ | -6.6 | -6.1 | -5.2 | -6.0 |
| $\mathrm{CH}_{2} \mathrm{JSC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH} \rightarrow \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{OH}$ | -7.1 | -7.5 | -6.7 | -7.1 |
| Average | -6.5 | -6.6 | -5.7 | -6.3 |
| $\mathrm{Hf}=-5.7$, use the average value of the CBS-QB3 level |  |  |  |  |
| $\mathbf{C H}_{3} \mathbf{S C}(=\mathbf{O}) \mathrm{CH}_{2} \mathbf{j}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CjO}$ | -3.3 | -3.4 | -2.9 | -3.2 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CHjCHO}$ | -2.4 | -2.9 | -3.5 | -2.9 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SCC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CHO}$ | -4.8 | -4.8 | -2.9 | -4.2 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{CHO}$ | -4.0 | -4.4 | -3.7 | -4.1 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{CHO} \rightarrow \mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CjO}$ | -5.5 | -5.2 | -4.8 | -5.2 |
| Average | -4.0 | -4.1 | -3.5 | -3.9 |
| $\mathrm{Hf}=-3.5$, 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 $\Delta_{f} \mathrm{H}^{0}(298)$ value is obtained from five work reactions. Bond energies for the formation of radicals reported at 298 K are calculated from the absolute $\Delta \mathrm{H}^{\mathrm{o}}{ }_{f 298}$ values of the parent molecules and radicals are from the average CBS-QB3 level calculations. The work reactions here use the corresponding $\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{O}}(298)$ of the radical and the parent and that of the hydrogen atom, $52.1 \mathrm{kcal} \mathrm{mol}^{-1}$. The $\mathrm{C}-\mathrm{H}$ bond energies of the parent molecules are summarized in Table 2.3. The $\Delta$ Hrxn of the reaction below is used to define the bond energy:

$$
\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}(298) \text { Parent }=\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{O}}(298) \text { Radical }+\mathrm{H} \text { atom }
$$

The bond energies of $\mathrm{H}-\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{SCH}(--\mathrm{H}) \mathrm{CHO}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{C}(=\mathrm{O})--\mathrm{H}$ are calculated using the reactions below:
$\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO} \rightarrow \mathrm{H} \bullet+\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO}$, $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO} \rightarrow \mathrm{H} \bullet+\mathrm{CH}_{3} \mathrm{SCHjCHO}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO} \rightarrow \mathrm{H} \bullet+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}$, respectively.

Similarly, the bond energies of $\mathrm{H}--\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{SCHO}, \mathrm{CH}_{3} \mathrm{CH}(--\mathrm{H}) \mathrm{SCHO}$, and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SC}(=\mathrm{O})--\mathrm{H}$ in $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$, and the bond energies of $\mathrm{H}-\mathrm{CH}_{2} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{C}(--\mathrm{H}) \mathrm{H}_{2}$ in $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ 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 ( $\mathrm{kcal} / \mathrm{mol}$ ).

| Parent |  | Radical |  |  | Bond Energy |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathbf{C H O}$ | = | C• $\mathrm{H}_{2} \mathrm{SCH}_{2} \mathrm{CHO}$ | + | H- | $\mathrm{CH}_{2}(--\mathrm{H}) \mathrm{SCH}_{2} \mathbf{C H O}$ |
| -34.9 |  | 8.4 |  | 52.1 | $8.4+52.1-(-34.9)=95.4$ |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathbf{C H O}$ | = | $\mathrm{CH}_{3} \mathrm{SC} \cdot \mathrm{HCHO}$ | + | H. | $\mathrm{CH}_{3} \mathrm{SCH}(--\mathrm{H}) \mathrm{CHO}$ |
| -34.9 |  | -3.3 |  | 52.1 | $-3.3+52.1-(-34.9)=83.7$ |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathbf{C H O}$ | = | $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{C} \cdot=0$ | + | H- | $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathbf{C}(-\mathrm{H})=\mathbf{O}$ |
| -34.9 |  | 4.8 |  | 52.1 | $4.8+52.1-(-34.9)=91.8$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathbf{S C H O}$ | = | C• $\mathrm{H}_{2} \mathrm{CH}_{2} \mathrm{SCHO}$ | + | H• | $\mathrm{CH}_{2}(--\mathrm{H}) \mathrm{CH}_{2} \mathbf{S C H O}$ |
| -43.0 |  | 5.4 |  | 52.1 | 5.4+52.1-(-43.0) = 100.5 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ | = | $\mathrm{CH}_{3} \mathrm{C} \cdot \mathrm{HSCHO}$ | + | H• | $\mathrm{CH}_{3} \mathbf{C H}(-\mathrm{H}) \mathrm{SCHO}$ |
| -43.0 |  | 0.9 |  | 52.1 | 0.9+52.1-(-43.1) = 96.0 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathbf{S C H O}$ | = | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SC} \cdot=0$ | + | H- | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathbf{S C}(-\mathrm{H})=\mathbf{0}$ |
| -43.0 |  | -5.1 |  | 52.1 | $-5.1+52.1-(-43.1)=90.0$ |
| $\mathrm{CH}_{3} \mathrm{SC}(=0) \mathrm{CH}_{3}$ | = | $\mathrm{C} \cdot \mathrm{H}_{2} \mathrm{SC}=\mathrm{OCH}_{3}$ | + | H- | $\mathrm{CH}_{2}(-\mathrm{H}) \mathrm{SC}(=0) \mathrm{CH}_{3}$ |
| -50.1 |  | -5.7 |  | 52.1 | $-5.7+52.1-(-50.1)=96.5$ |
| $\mathrm{CH}_{3} \mathrm{SC}(=0) \mathrm{CH}_{3}$ | = | $\mathrm{CH}_{3} \mathrm{SC}=\mathrm{OC} \cdot \mathrm{H}_{2}$ | + | H- | $\mathbf{C H}_{3} \mathbf{S C}(=0) \mathrm{CH}_{2}(-\mathrm{H})$ |
| -50.1 |  | -3.5 |  | 52.1 | $-3.5+52.1-(-50.1)=98.7$ |

Bond Energies: $\mathrm{H}-\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO} \quad \mathrm{CH}_{3} \mathrm{SCH}(-\mathrm{H}) \mathrm{CHO} \quad \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{C}(-\mathrm{H})=\mathrm{O}$
95.4,
83.7
91.8
$\mathrm{kcal} / \mathrm{mol}$.

Bond Energies: $\mathrm{H}-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{SCHO}$
$\mathrm{CH}_{3} \mathrm{CH}(-\mathrm{H}) \mathrm{SCHO}$
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SC}(-\mathrm{H}) \mathrm{O}$
$100.5 \quad 96.0 \quad 90.0 \quad \mathrm{kcal} / \mathrm{mol}$.

Bond Energies :

$$
\mathrm{H}-\mathrm{CH}_{2} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}
$$

$\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2}-\mathrm{H}$

### 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 $0^{\circ}$ to $360^{\circ}$ in steps of $15^{\circ}$, 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) $\mathrm{CH} 3--\mathrm{SCH} 2 \mathrm{CHO}$

(b) $\mathrm{CH}_{3} \mathrm{~S}--\mathrm{CH}_{2} \mathrm{CHO}$

(c) $\mathrm{CH}_{3} \mathrm{SCH}_{2}-\mathrm{CHO}$

Figure 2.4 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ at UB3LY/3-21G level.


(c) $\mathrm{CH}_{2} \mathrm{SCH}_{2}-$ - CHO

Figure 2.5 Potential energy barriers for internal rotations in $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO}$ at UB3LY/3-21G level.


Figure 2.6 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SCHjCHO}$ at UB3LY/3-21G level.

(a) $\mathrm{CH}_{3} \mathrm{~S}--\mathrm{CH}_{2} \mathrm{Cj}=\mathrm{O}$

(b) $\mathrm{CH}_{3} \mathrm{SCH}_{2}-\mathrm{Cj}=\mathrm{O}$

Figure 2.7 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{Cj}=\mathrm{O}$ at UB3LY/3-21G level.
$\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ has the internal rotors of $\mathrm{C}-\mathrm{SCC}(=\mathrm{O}), \mathrm{CS}-\mathrm{CC}(=\mathrm{O})$ and $\mathrm{CSC}-$ $\mathrm{C}(=\mathrm{O})$, as demonstrated in Figure 2.4 (a), (b) and (c) respectively, their barriers are respectively $2,5.5$ and $5.4 \mathrm{kcal} / \mathrm{mol}$. The first radical, $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO}$, has the rotators of $\mathrm{Cj}-\mathrm{SCC}(=\mathrm{O}), \mathrm{CjS}-\mathrm{CC}(=\mathrm{O})$ and $\mathrm{CjSC}-\mathrm{C}(=\mathrm{O})$, and their barriers are $5,5.3$ and 4.4, respectively, as shown in Figure 2.5 (a), (b) and (c). The second radical, $\mathrm{CH}_{3} \mathrm{SCHjCHO}$, the barriers of its following rotators: $\mathrm{CS}-\mathrm{CjC}(=\mathrm{O})$ and $\mathrm{CSCj}-\mathrm{C}(=\mathrm{O})$ are 12 and 22 $\mathrm{kcal} / \mathrm{mol}$, as in Figure 2.6 (a) and (b). Then the third radical, $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}$, the barriers of its rotators of $\mathrm{CS}-\mathrm{CC}(=\mathrm{O}) \mathrm{j}$ and $\mathrm{CSC}-\mathrm{C}(=\mathrm{O}) \mathrm{j}$ are 3.7 and $5.4 \mathrm{kcal} / \mathrm{mol}$, it's shown in Figure 2.7 (a) and (b).


Figure 2.8 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ at UB3LY/3-21G level.


Figure 2.9 Potential energy barriers for internal rotations in $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}$ at UB3LY/3-21G level.

(a) CH3--CHjSCHO

(b) $\mathrm{CH}_{3} \mathrm{CHj}-\mathrm{SCHO}$

(c) $\mathrm{CH}_{3} \mathrm{CHjS}-\mathrm{CHO}$

Figure 2.10 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{CHjSCHO}$ at UB3LY/3-21G level.


Figure 2.11 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCj}=\mathrm{O}$ at UB3LY/3-21G level.

For the parent molecule of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ in Figure 2.8, its rotor of $\mathrm{CC}-\mathrm{SC}(=\mathrm{O})$ and $\mathrm{CCS}-\mathrm{C}(=\mathrm{O})$ are 5.3 and $13.3 \mathrm{kcal} / \mathrm{mol}$, as seen respectively in Figure 2.8 (a) and (b). The first radical in Figure $2.9, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{SCHO}$, its rotor of $\mathrm{Cj}-\mathrm{CSC}(=\mathrm{O})$ is $4.5 \mathrm{kcal} / \mathrm{mol}$. The second radical, $\mathrm{CH}_{3} \mathrm{CHjSCHO}$, its rotors are $\mathrm{C}-\mathrm{CjSC}(=\mathrm{O}), \mathrm{CCj}-$ $\mathrm{SC}(=\mathrm{O})$ and $\mathrm{CCjS}-\mathrm{C}(=\mathrm{O})$, their barriers are respectively 0.22 , 4 and $11.8 \mathrm{kcal} / \mathrm{mol}$, as demonstrated in Figure 2.10 (a), (b) and (c). The third radical, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}$, the barriers of its rotors of $\mathrm{CC}-\mathrm{SC}(=\mathrm{O}) \mathrm{j}$ and $\mathrm{CCS}-\mathrm{C}(=\mathrm{O}) \mathrm{j}$ are 3 and $14 \mathrm{kcal} / \mathrm{mol}$, as in Figure 2.11 (a) and (b).


Figure 2.12 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ at UB3LY/3-21G level.


Figure 2.13 Potential energy barriers for internal rotations in $\mathrm{CH}_{2} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ at UB3LY/3-21G level.


Figure 2.14 Potential energy barriers for internal rotations in $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}$ at UB3LY/3-21G level.

Then, for $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$, its rotors of $\mathrm{CS}-\mathrm{C}(=\mathrm{O}) \mathrm{C}$ and $\mathrm{CSC}(=\mathrm{O})-\mathrm{C}$ are 12 and $0.18 \mathrm{kcal} / \mathrm{mol}$ as in Figure 2.12 (a) and (b). Its first radical, $\mathrm{CH}_{2} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$, the rotors of $\mathrm{Cj}-\mathrm{SC}(=\mathrm{O}) \mathrm{C}$ and $\mathrm{CjS}-\mathrm{C}(=\mathrm{O}) \mathrm{C}$, their barriers are 5.8 and $9.9 \mathrm{kcal} / \mathrm{mol}$, as in Figure 2.13 (a) and (b). Then its second radical, $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2}$ j, its rotors of $\mathrm{CS}-$ $\mathrm{C}(=\mathrm{O}) \mathrm{Cj}$ and $\operatorname{CSC}(=\mathrm{O})-\mathrm{Cj}$, the barriers are 10.8 and $10.6 \mathrm{kcal} / \mathrm{mol}$, as in Figure 2.14 (a) and (b).

### 2.2.6 $\mathrm{S}^{\circ} 298$ and $\mathrm{Cp}^{\circ}(\mathbf{T})$

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 298 K entropy and heat capacity vs. temperature of parent $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ 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 $1-5000 \mathrm{~K}$. All these data are ideal gas thermodynamic properties at standard state ( $\mathrm{P}=1 \mathrm{~atm}$ and $\mathrm{T}=298 \mathrm{~K}$ ). 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 | $\mathrm{S}^{\circ}$ 298K | Cp300 | Cp400 | Cp500 | Cp600 | Cp800 | Cp1000 | Cp1500 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ | 80.3 | 23.2 | 28.1 | 32.4 | 36.1 | 41.9 | 46.1 | 52.6 |
| $\mathrm{CH}_{2} \mathrm{jSCH}_{2} \mathrm{CHO}$ | 79.6 | 24.0 | 28.3 | 32.0 | 35.0 | 39.6 | 43.0 | 48.2 |
| $\mathrm{CH}_{3} \mathrm{SCHjCHO}$ | 78.6 | 22.3 | 26.9 | 30.8 | 34.0 | 39.0 | 42.6 | 48.0 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{Cj}=\mathrm{O}$ | 80.1 | 23.0 | 27.4 | 31.1 | 34.2 | 39.0 | 42.5 | 48.0 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ | 79.0 | 22.8 | 27.8 | 32.1 | 35.8 | 41.7 | 45.9 | 52.5 |
| $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}$ | 77.9 | 23.6 | 28.1 | 31.8 | 34.8 | 39.5 | 42.9 | 48.2 |
| $\mathrm{CH}_{3} \mathrm{CHjSCHO}$ | 81.3 | 23.4 | 27.6 | 31.3 | 34.4 | 39.2 | 42.7 | 48.2 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}$ | 79.4 | 22.8 | 27.0 | 30.6 | 33.8 | 38.7 | 42.3 | 47.9 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ | 81.1 | 24.0 | 28.7 | 32.8 | 36.4 | 42.0 | 46.1 | 52.5 |
| $\mathrm{CH}_{2} \mathrm{jSC}(=\mathrm{O}) \mathrm{CH}_{3}$ | 80.1 | 24.6 | 28.8 | 32.3 | 35.2 | 39.7 | 43.0 | 48.2 |
| $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{j}$ | 78.9 | 23.8 | 28.2 | 31.9 | 34.9 | 39.5 | 42.9 | 48.1 |

### 2.3 Summary

Thermochemical parameters $\Delta_{\mathrm{f}} \mathrm{H}^{\circ}(298)$, standard entropy at 298.15 K and entropy and heat capacities form 1 to 5000 K are presented for the lowest energy conformers of three proposed main products of atmospheric methyl ethyl partial oxidation: $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$, 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$31 \mathrm{G}(\mathrm{d}, \mathrm{p})$ and $6-31+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})$ basis sets and work reactions with bond balance work well for these sulfur carbonyl species. The recommended Enthalpies of formation for $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ are -34.9, -43.0 and -50.1 kcal/mol respectively. $\mathrm{C}-\mathrm{H}$ 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 $\mathrm{O}_{2}$

## Overview

The structure and thermochemical parameters $\left(\Delta_{f} \mathrm{H}^{\circ}(298), \mathrm{S}^{0}\right.$ and $\left.\mathrm{Cp}(\mathrm{T})\right)$, 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$31 \mathrm{G}(\mathrm{d}, \mathrm{p})$, 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 $\operatorname{CCSD}(\mathrm{T})$ 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 $(298 \mathrm{~K})$ 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 ( $\mathrm{S}^{\circ}(\mathrm{T})$ and $\left.\mathrm{Cp}^{\circ}(\mathrm{T})\right)$ are calculated using the "SMCPS" (Statistical Mechanics for Heat Capacity and Entropy $\underline{C p}$ and $\underline{S}$ ) program which incorporates data on the frequencies, moments of inertia, molecular mass, symmetry and number of optical isomers from the B3LYP/6$31 \mathrm{G}(2 \mathrm{~d}, 2 \mathrm{p})$ 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) $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{C}=-70.7^{\circ}$

(b) $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{C}=-70.6^{\circ}$

(c) $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$
-C-C =36.3

Figure 3.1 Optimized structures of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ at CBS-QB3 level (Bond distances in $\AA$; Bond Angles in ${ }^{\circ}$ ).

In $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$, as shown in Figure 3.1 (a), all the $\mathrm{H}-\mathrm{C}$ bonds are also $1.1 \pm 0.02 \mathrm{~A}^{\circ}$, both the $\mathrm{C}-\mathrm{SCC}$ bond and $\mathrm{CS}-\mathrm{CC}$ bond are 1.82 and $1.83 \mathrm{~A}^{\circ}, \mathrm{CSC}-\mathrm{C}$ is $1.53 \mathrm{~A}^{\circ}$. The $\mathrm{C}-\mathrm{S}-\mathrm{CC}$ angle is $101.0^{\circ}$, the $\mathrm{CS}-\mathrm{C}-\mathrm{C}$ angle is $115.1^{\circ}$.

Then, for the radicals: 1) in $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$, as shown in Figure 3.1 (b), there is no evident change in the lengths of all the $\mathrm{C}-\mathrm{H}$ bonds and each internal bond angle, but the bond of $\mathrm{C}-\mathrm{SCC}$ has shortened to $1.72 \mathrm{~A}^{\circ}$; 2)in $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$, as shown in Figure 3.1 (c), the angle of $\mathrm{C}-\mathrm{S}-\mathrm{CC}$ has increased to $103.8^{\circ}, \mathrm{CS}-\mathrm{C}-\mathrm{C}$ has evidently increased to $125.0^{\circ}$, and CS-CC has shortened to $1.73 \mathrm{~A}^{\circ}$, but there is also no evident change in
each $\mathrm{C}-\mathrm{H}$ bond; 3) in $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$, as shown in Figure 3.1 (d), $\mathrm{CS}-\mathrm{C}-\mathrm{C}$ has undergone minor decrease to $113.0^{\circ}$ and CS-CC has increased to $1.88 \mathrm{~A}^{\circ}$.

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 $\mathrm{C}-\mathrm{S}$ bonds and $\mathrm{C}-\mathrm{H}$ bonds. Removal of an H atom on the methyl side of a sulfur atom will lead to formation a partial double bond: $\mathrm{C}_{-} \mathrm{SCC}$, 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 $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ : $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$, $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$. 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 $\mathrm{C}-\mathrm{H}$ bond length, and the other changes are similar to the formation of radicals from $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$. The bond between two O atoms decreases significantly from about $1.5 \mathrm{~A}^{\circ}$ to near $1.3 \mathrm{~A}^{\circ}$ 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 $\mathrm{RO}=\mathrm{O} \cdot$ double bond.

(a) $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$
$\mathrm{O}-\mathrm{O}-\mathrm{C}-\mathrm{S}=-173.5^{\circ} \quad \mathrm{O}-\mathrm{C}-\mathrm{S}-\mathrm{C}=72.6^{\circ}$
C-S-C-C $=-176.4^{\circ}$

(b) $\mathrm{jOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3} \quad \mathrm{O}-\mathrm{O}-\mathrm{C}-\mathrm{S}=162.2^{\circ} \quad \mathrm{O}-\mathrm{C}-\mathrm{S}-\mathrm{C}=-73.0^{\circ} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{C}=178.7^{\circ}$

(c) $\mathrm{HOOCH}_{2} \mathrm{SCHjCH}_{3}$
O-O-C-S =-178.8
O-C-S-C $=77.1^{\circ}$
C-S-C-C $=-172.1^{\circ}$

(d) $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$
$\mathrm{O}-\mathrm{O}-\mathrm{C}-\mathrm{S}=-72.4^{\circ}$
O-C-S-C $=104.7^{\circ}$
C-S-C-C $=-79.8^{\circ}$

Figure 3.2 Optimized structures of $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{jOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$,
$\mathrm{HOOCH}_{2} \mathrm{SCHjCH}_{3}$ and $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ at CBS-QB3 level (Bond distances in $\AA$; Bond Angles in ${ }^{\circ}$ ).


(d) $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2} \mathrm{j} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{C}=-168.4^{\circ} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{O}=69.7^{\circ} \quad \mathrm{S}-\mathrm{C}-\mathrm{O}-\mathrm{O}=-164.5^{\circ}$

Figure 3.3 Optimized structures of $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$, $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOj}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2} \mathrm{j}$ at CBS-QB3 level (Bond distances in $\AA$; Bond Angles in ${ }^{\circ}$ ).

(a) $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{C}=180^{\circ} \quad \mathrm{S}-\mathrm{C}-\mathrm{C}-\mathrm{O}=180^{\circ} \quad \mathrm{C}-\mathrm{C}-\mathrm{O}-\mathrm{O}=-180^{\circ}$

(b) $\mathrm{CH}_{2} \mathrm{jSCH}_{2} \mathrm{CH}_{2} \mathrm{OOH} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{C}=178.6^{\circ} \quad \mathrm{S}-\mathrm{C}-\mathrm{C}-\mathrm{O}=-178.6^{\circ} \quad \mathrm{C}-\mathrm{C}-\mathrm{O}-\mathrm{O}=-175.8^{\circ}$

(c) $\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{OOH} \quad \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{C}=178.5^{\circ} \quad \mathrm{S}-\mathrm{C}-\mathrm{C}-\mathrm{O}=81.7^{\circ} \quad \mathrm{C}-\mathrm{C}-\mathrm{O}-\mathrm{O}=67.1^{\circ}$


Figure 3.4 Optimized structures of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}, \mathrm{CH}_{2} \mathrm{jCCH} \mathrm{CH}_{2} \mathrm{OOH}$, $\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{OOH}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOj}$ at CBS-QB3 level (Bond distances in $\AA$; Bond Angles in ${ }^{\circ}$ ).

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 O 2 . Then, in the atmosphere, the peroxy radicals react with nitric oxide ( NO ) to form NO 2 and alkoxy radicals.
$\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}^{\bullet}+\mathrm{O} 2=\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OO}$ • and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OO} \cdot+\mathrm{NO}=\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{O} \bullet+\mathrm{NO} 2 \Delta \mathrm{HRxn}=-13 \mathrm{kcal} \mathrm{mol}^{-1}$

Sulfoxides are formed in atmospheric and combustion chemistry via reactions with OH radical and $\mathrm{O}_{2}$.
$\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{OH}=\mathrm{CH}_{3} \mathrm{~S} \bullet(-\mathrm{OH}) \mathrm{CH}_{2} \mathrm{CH}_{3} \quad$ and $\mathrm{CH}_{3} \mathrm{~S} \bullet(-\mathrm{OH}) \mathrm{CH}_{2} \mathrm{CH}_{3}+\mathrm{O}_{2}=\left[\mathrm{CH}_{3} \mathrm{~S} \bullet\left(\mathrm{OO} \bullet(-\mathrm{OH}) \mathrm{CH}_{2} \mathrm{CH}_{3}\right]=\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{CH}_{3}+\mathrm{HO}_{2}\right.$

The $\left[\mathrm{CH}_{3} \mathrm{~S} \bullet(-\mathrm{OH}) \mathrm{CH}_{2} \mathrm{CH}_{3}\right]$ and $\left[\mathrm{CH}_{3} \mathrm{~S} \bullet\left(\mathrm{OO} \bullet(-\mathrm{OH}) \mathrm{CH}_{2} \mathrm{CH}_{3}\right]\right.$ 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 $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}, \mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ and $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ are determined, and reported in Figure 3.5-3.8.


C-S-C-O $=180^{\circ}$
Figure 3.5 Optimized structure of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$ at CBS-QB3 level (Bond distances in A; Bond Angles in ${ }^{\circ}$ ).


Figure 3.6 Optimized structure of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}$ at $\mathrm{CBS}-\mathrm{QB} 3$ level (Bond distances in $\AA$; Bond Angles in ${ }^{\circ}$ ).

$\mathrm{O}-\mathrm{C}-\mathrm{S}=\mathrm{O}=176.5^{\circ}$, O-C-S-C $=66.2^{\circ}$
Figure 3.7 Optimized structure of $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ at $\mathrm{CBS}-\mathrm{QB} 3$ level (Bond distances in A; Bond Angles in ${ }^{\circ}$ ).


C-C-S-C $=-164.2^{\circ}, \mathrm{C}-\mathrm{C}-\mathrm{S}=\mathrm{O}=88.2^{\circ}, \mathrm{C}-\mathrm{S}-\mathrm{C}-\mathrm{O}=74.0^{\circ}$
Figure 3.8 Optimized structure of $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ at $\mathrm{CBS}-\mathrm{QB} 3$ level (Bond distances in $\AA$; Bond Angles in ${ }^{\circ}$ ).

In Figure 3.8, it can be seen that at the lowest energy point of $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$, 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 $\Delta_{f} H^{\circ}(298)$ of the target parent and radical intermediates have been determined using calculated $\Delta_{f} H^{0}(298)$ values for each species, then calculating the $\Delta$ Hreaction at 298 K , and then using the known literature values for the three reference molecules in the work reaction and the calculated $\Delta \mathrm{Hrxn}$ find $\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}(298)$ of the target. The standard enthalpies of formation of the reference species at 298 K 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.

$$
\Delta \mathrm{Hrxn}=\Sigma \Delta_{\mathrm{f}} \mathrm{H}^{0}(298) \text { products }-\Sigma \Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}} \text { (298) reactants }
$$

The work reactions in Table 3.2 are used to calculate the heat of reaction and enthalpies of formation for the stable molecules of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}, \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$, $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$, 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: $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}$, $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ and $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$. 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
$\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}(298)$, as this method has the highest accuracy. $\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{O}}(298)$ 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 $\mathrm{C}-\mathrm{H}$ 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 | $\Delta \mathbf{H}^{\text {+ }}{ }^{\text {298 }}$ ( $\mathrm{kcal} \mathrm{mol}^{-1}$ ) | Reference |
| :---: | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{CH}_{3}$ | -20.04 | [14] |
| $\mathrm{CH}_{3} \mathrm{SCH}_{3}$ | -8.96 | [8] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3}$ | -24.82 | [14] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | -20 | [12] |
| $\mathrm{CH}_{2} \mathrm{CHH}_{3}$ | 29.1 | [18] |
| $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}$ | 23.67 | [8] |
| $\mathrm{CH}_{3} \mathrm{CHjCH}_{3}$ | 21.02 | [8] |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{3}$ | -35.97 | [16] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{3}$ | -41.77 | [16] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SH}$ | -11.03 | [12] |
| $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}$ | -49.93 | [17] |
| $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOH}) \mathrm{SH}$ | -36.29 | [11] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OOH}$ | -40.1 | [17] |
| $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOj}) \mathrm{CH}_{3}$ | -15.2 | [17] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OOj}$ | -6.72 | [5] |
| $\mathrm{CH}_{2} \mathrm{CHH}_{2} \mathrm{OOH}$ | 10.9 | [5] |
| $\mathrm{CH}_{2} \mathrm{jCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ | 1.6 | [5] |
| $\mathrm{CH}_{2} \mathrm{jSCH}_{3}$ | 32.66 | [11] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ | -46.56 | [11] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOj}$ | -12.62 | [11] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ | -56.23 | [8] |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | -61.13 | [8] |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$ | -41.6 | This work |
| CH3CH2SCH2OH | -52.8 | This work |

Table 3.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation ( $\Delta \mathrm{H}^{\mathrm{o}} \mathrm{f} 298$ ) of the Parents and the Radicals ${ }^{\mathrm{a}}$ (Units: $\left.\mathrm{kcal} / \mathrm{mol}\right)^{\text {a }}$.

| Work Reactions | $\Delta \mathbf{H}_{\mathrm{f}}{ }_{298}\left(\mathrm{kcal} \mathrm{mol}{ }^{-1}\right)$ |  | CBS- <br> QB3 | Average |
| :---: | :---: | :---: | :---: | :---: |
|  | $\begin{aligned} & \text { b31yp/6- } \\ & \mathbf{3 1 G}(\mathbf{d}, \mathbf{p}) \end{aligned}$ | $\begin{aligned} & \text { b31yp/6- } \\ & 31+G(2 d, p) \end{aligned}$ |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{3}$ | -15.0 | -15.0 | -14.7 | -14.9 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{3} \quad \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3}$ | -14.0 | -14.0 | -14.4 | -14.1 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | -14.5 | -14.5 | -14.5 | -14.5 |
| Average of all the work reactions | -14.5 | -14.5 | -14.5 | -14.5 |
| $\mathrm{Hf}=-14.5$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathbf{C H}_{2} \mathbf{j S C H}_{2} \mathbf{C H}_{3}$ |  |  |  |  |
| $\mathrm{CH}_{2} \mathrm{j} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{jCH}_{3}$ | 27.1 | 26.4 | 26.8 | 26.8 |
| $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}$ | 27.3 | 26.6 | 25.7 | 26.5 |
| $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CHjCH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | 28.3 | 27.3 | 26.5 | 27.4 |
| $\mathrm{CH}_{2} \mathrm{j} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | 26.7 | 26.1 | 25.6 | 26.2 |
| Average | 27.3 | 26.6 | 26.2 | 26.7 |
| $\mathrm{Hf}=26.2$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{jCH}_{3}$ | 25.5 | 25.3 | 26.5 | 25.8 |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}$ | 25.7 | 25.5 | 25.5 | 25.5 |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CHjCH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | 26.7 | 26.2 | 26.2 | 26.4 |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | 25.2 | 24.9 | 25.4 | 25.2 |
| Average | 25.8 | 25.5 | 25.9 | 25.7 |
| $\mathbf{H f}=25.9$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2 \mathrm{j}}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{2} \mathrm{jCH}_{3}$ | 32.5 | 32.6 | 33.9 | 33.0 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{CH}_{3} \quad \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}$ | 32.7 | 32.8 | 32.8 | 32.8 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2 \mathrm{j}}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CHjCH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | 33.8 | 33.5 | 33.5 | 33.6 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | 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 |  |  |  |  |
| $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ |  |  |  |  |
| $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SH} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOH}) \mathrm{SH}$ | -37.1 | -37.9 | -36.4 | -37.1 |
| $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}$ | -35.4 | -36.1 | -35.3 | -35.6 |
| Average | -36.2 | -37.0 | -35.8 | -36.4 |
| $\mathrm{Hf}=-\mathbf{3 5 . 8}$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{jOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OOH}-\rightarrow \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OOj}$ | 3.3 | 3.4 | -2.0 | 1.6 |
| $\mathrm{jOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH} \rightarrow \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOj}$ | 3.9 | 4.0 | -1.7 | 2.1 |
| Average | 3.6 | 3.7 | -1.8 | 1.8 |
| $\mathrm{Hf}=-1.8$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{HOOCH}_{2} \mathrm{SCHjCH}_{3}$ |  |  |  |  |
| $\mathrm{HOOCH} 2 \mathrm{SCHjCH} 3+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ | 4.6 | 5.1 | 5.0 | 4.9 |
| $\mathrm{HOOCH} 2 \mathrm{SCHjCH} 3+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ | 4.8 | 4.9 | 4.8 | 4.9 |
| Average | 4.7 | 5.0 | 4.9 | 4.9 |
| $\mathrm{Hf}=4.9$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ |  |  |  |  |
| $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ | 9.3 | 10.2 | 10.5 | 10.0 |
| $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ | 9.1 | 10.3 | 10.6 | 10.0 |
| Average | 9.2 | 10.2 | 10.5 | 10.0 |
| $\mathbf{H f}=10.5$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SH} \rightarrow \mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOH}) \mathrm{SH}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | -40.5 | -40.4 | -40.5 | -40.5 |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{3}$ | -38.8 | -38.6 | -39.4 | -38.9 |
| Average | -39.7 | -39.5 | -39.9 | -39.7 |
| $\mathrm{Hf}=-39.9$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{2} \mathrm{jSCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ |  |  |  |  |
| $\mathrm{CH}_{2} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH} 2 \mathrm{jSCH} 2 \mathrm{CH} 3+$ | 3.5 | 3.8 | 3.9 | 3.7 |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ | 3.0 | 3.6 | 3.7 | 3.4 |
| $\mathrm{CH}_{2} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{3} \rightarrow \mathrm{CH} 2 \mathrm{jSCH} 3+\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ | 3.2 | 3.7 | 3.8 | 3.6 |
| Average |  |  |  |  |
| $\mathbf{H f}=3.8$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOj}) \mathrm{CH}_{3}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOj}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOj}) \mathrm{C}$ | -3.8 | -4.0 | -4.2 | -4.0 |
| $\mathrm{H}_{3}$ | -5.3 | -5.5 | -6.0 | -5.6 |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOj}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OOH}--\rightarrow \mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OOj}$ | -4.6 | -4.8 | -5.1 | -4.8 | Average

$\mathrm{Hf}=-5.1$, the average of the CBS-QB3 level

Table 3.2 Enthalpies of Reaction at 298 K and Calculated Enthalpies of Formation $\left(\Delta \mathrm{H}^{\mathrm{f} 298}\right.$ ) of the Parents and the Radicals ${ }^{\mathrm{a}}$ (Units: kcal/mol) ${ }^{\text {a }}$. (Continued)

| Work Reactions | $\Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{o}}{ }_{298}\left(\mathrm{kcal} \mathrm{mol}{ }^{-1}\right)$ |  | CBS- <br> QB3 | Average |
| :---: | :---: | :---: | :---: | :---: |
|  | b3lyp/6- <br> 31G(d,p) | b3lyp/6-31+G(2d,p) |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2} \mathbf{j}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2 \mathrm{j}}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{2} \mathrm{CHH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | 12.1 | 12.9 | 11.8 | 12.3 |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2} \mathrm{j}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{2} \mathrm{j} \mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{3}$ | 11.8 | 12.0 | 11.6 | 11.8 |
| Average | 11.9 | 12.5 | 11.7 | 12.0 |
| $\mathrm{Hf}=11.7$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SH} \rightarrow \mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOH}) \mathrm{SH}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | -35.0 | -35.7 | -34.7 | -35.1 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{3}$ | -33.3 | -33.9 | -33.6 | -33.6 |
| Average | -34.2 | -34.8 | -34.2 | -34.4 |
| $\mathbf{H f}=-34.2$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathbf{C H}_{2} \mathbf{j S C H}_{2} \mathrm{CH}_{2} \mathbf{O O H}$ |  |  |  |  |
| $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OOH}$ | 9.7 | 9.7 | 9.2 | 9.6 |
| $\mathrm{CH}_{2} \mathrm{SCH} \mathrm{SCH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{2} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ | 7.8 | 8.0 | 7.5 | 7.8 |
| Average | 8.8 | 8.9 | 8.3 | 8.7 |
| $\mathrm{Hf}=8.3$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{OOH}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}+$ | 3.5 | 3.0 | 3.9 | 3.4 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ | 3.3 | 3.1 | 4.0 | 3.4 |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ | 3.0 | 3.0 | 3.9 | 3.4 |
| Average |  |  |  |  |
| $\mathbf{H f}=3.9$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOj}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOj}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OOH} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OOj}$ | -0.7 | -0.8 | -0.4 | -0.7 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOj}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{O}$ | -0.2 | -0.2 | -0.1 | -0.1 |
| OH | -0.5 | -0.5 | -0.3 | -0.4 |
| Average |  |  |  |  |
| $\mathbf{H f}=-0.3$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ | -40.8 | -40.7 | -41.8 | -41.1 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | -40.5 | -40.6 | -41.6 | -40.9 |
| Average | -40.6 | -40.7 | -41.6 | -41.0 |
| $\mathrm{Hf}=-41.6$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | -53.4 | -52.7 | -53.0 | -53.0 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | -53.4 | -52.7 | -52.6 | -52.9 |
| Average | -53.4 | -52.7 | -52.8 | -53.0 |
| $\mathrm{Hf}=-52.8$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{SCH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{3}$ | -72.9 | -71.3 | -69.8 | -71.4 |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{3}$ | -72.0 | -71.2 | -70.8 | -71.3 |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{3}$ | -72.3 | -71.1 | -69.6 | -71.0 |
| Average | -72.4 | -71.2 | -70.1 | -71.2 |
| $\mathrm{Hf}=-70.1$, the average of the CBS-QB3 level |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{3}$ | -86.7 | -83.7 | -84.8 | -85.1 |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{3}$ | -87.0 | -83.6 | -83.6 | -84.7 |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}+$ | -86.1 | -83.5 | -84.5 | -84.7 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{3}$ | -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 $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ Calculated in $\mathrm{kcal} / \mathrm{mol}$

## Bond Energy:



## Bond energies:

| $\mathrm{CH}_{2}(-\mathrm{H}) \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | $92.8 \mathrm{kcal} / \mathrm{mol}$ |
| :--- | :--- |
| $\mathrm{CH}_{3} \mathrm{SCH}(--\mathrm{H}) \mathrm{CH}_{3}$ | $92.5 \mathrm{kcal} / \mathrm{mol}$ |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}-\mathrm{H}$ | $99.7 \mathrm{kcal} / \mathrm{mol}$ |

### 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 $\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}(298)$ 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 $\Delta \mathrm{H}_{f 298}^{0}$ values of the parent molecules and radicals are from the average CBS-QB3 level calculations. The work reactions here use the corresponding $\Delta_{f} \mathrm{H}^{\circ}(298)$ of the radical and the parent and that of the hydrogen atom, 52.1 $\mathrm{kcal} / \mathrm{mol}$. The $\mathrm{C}-\mathrm{H}$ bond energies of the parent molecules are summarized in Table 3.3 and Table 3.4. The $\Delta H r x n$ of the reaction below is used to define the bond energy:

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

The bond energies of $\mathrm{H}-\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCH}(--\mathrm{H}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}--$ H are calculated respectively using the reactions below:
$\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{H} \bullet+\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$
$\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{H} \bullet+\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$
and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3} \rightarrow \mathrm{H} \bullet+\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}$, respectively

The values are $92.8,92.5$ and $99.7 \mathrm{kcal} / \mathrm{mol}$ respectively, as shown in Table 3.3.
In Table 3.4, similar work reactions and methods were applied to calculate the targeted $\mathrm{C}-\mathrm{H}$ or $\mathrm{OO}-\mathrm{H}$ bond energies of the species containing one $\mathrm{C}-\mathrm{OOH}$ group in each molecule. It's evident that in each molecule the $\mathrm{H}-\mathrm{X}(\mathrm{X}=\mathrm{C}, \mathrm{O})$ bond on the peroxide group is the weakest, at the same time that on the carbon farthest to sulfur is the highest.

Table $3.4 \mathrm{H}-\mathrm{X}(\mathrm{X}=\mathrm{C}, \mathrm{O})$ Bond Energies of $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ Calculated in $\mathrm{kcal} / \mathrm{mol}$

## Bond Energy

| - $\mathrm{OOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | $+\mathrm{H}^{\bullet}$ | $=\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | $\mathrm{H}--\mathrm{OOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ |
| :---: | :---: | :---: | :---: |
| -1.8 | 52.1 | -35.8 | $-1.8+52.1-(-35.8)=86.1$ |
| $\mathrm{HOOCH}_{2} \mathrm{SC} \cdot \mathrm{HCH}_{3}$ | $+\mathrm{H} \cdot$ | $=\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | $\mathrm{H}_{3}$ |
| 4.9 | 52.1 | -35.8 | $4.9+52.1-(-35.8)=92.8$ |
| $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{C} \cdot \mathrm{H}_{2}$ | $+\mathrm{H} \cdot$ | $=\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | $\mathrm{OOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2}(--\mathrm{H})$ |
| 10.5 | 52.1 | -35.8 | $10.5+52.1-(-35.8)=98.4$ |
| C | $+\mathrm{H}$ | ${ }_{3}$ | ${ }_{3}$ |
| 3.8 | 52.1 | -39.9 | $3.8+52.1-(-39.9)=95.8$ |
| $\mathrm{CH}_{3}$ | $+\mathrm{H} \cdot$ | $=$ | $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OO}--\mathrm{H}) \mathrm{CH}_{3}$ |
| -5.1 | 52.1 | -39.9 | $-5.1+52.1-(-39.9)=86.9$ |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{C} \cdot \mathrm{H}_{2}$ | + H | H) $\mathrm{CH}_{3}$ | $\mathrm{H}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2}(--\mathrm{H})$ |
| 11.7 | 52.1 | -39.9 | $11.7+52.1-(-39.9)=103.7$ |
| $\mathrm{C} \cdot \mathrm{H}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ | $+\mathrm{H} \cdot$ | $=\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ | $\mathrm{CH}_{2}(--\mathrm{H}) \mathrm{SCH} 2 \mathrm{CH} 2 \mathrm{OOH}$ |
| 8.3 | 52.1 | -34.2 | $8.3+52.1-(-34.2)=94.6$ |
| $\mathrm{CH}_{3} \mathrm{SC} \cdot \mathrm{HCH}_{2} \mathrm{OOH}$ | $+\mathrm{H} \cdot$ | $=\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ | $\mathrm{CH}_{3} \mathrm{SCH}(--\mathrm{H}) \mathrm{CH}_{2} \mathrm{OOH}$ |
| 3.9 | 52.1 | -34.2 | $3.9+52.1-(-34.2)=90.2$ |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OO}$ - | $+\mathrm{H}^{\bullet}$ | $=\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ | $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OO}-\mathrm{H}$ |
| -0.3 | 52.1 | -34.2 | $-0.3+52.1-(-34.2)=86$. |

## Bond energies:

$\mathrm{H}--\mathrm{OOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3} \quad \mathrm{HOOCH}_{2} \mathrm{SCH}(--\mathrm{H}) \mathrm{CH}_{3} \quad \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2}(--\mathrm{H})$

| 86.1 | 92.8 | 98.4 | $\mathrm{kcal} / \mathrm{mol}$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{CH}_{2}(--\mathrm{H}) \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ | $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OO}--\mathrm{H}) \mathrm{CH}_{3}$ | $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2}(--\mathrm{H})$ |  |
| 95.8 | 86.9 | 103.7 | $\mathrm{kcal} / \mathrm{mol}$ |
| $\mathrm{CH}_{2}(--\mathrm{H}) \mathrm{SCH} 2 \mathrm{CH} 2 \mathrm{OOH}$ | $\mathrm{CH}_{3} \mathrm{SCH}(--\mathrm{H}) \mathrm{CH}_{2} \mathrm{OOH}$ | $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OO}-\mathrm{H}$ |  |
| 94.6 | 90.2 | 86.0 | $\mathrm{kcal} / \mathrm{mol}$ |

### 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 $0^{\circ}$ to $360^{\circ}$ in steps of $15^{\circ}$.

In Figure 3.9 (a), (b), (c) and (d), those for $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{j} \mathrm{SCH}_{2} \mathrm{CH}_{3}$, $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ 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.


Figure 3.9 Potential energy barriers for internal rotations of the CS—CC bond in $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}$ at B3LYP/6-31G(d, p) , B3LYP/6-31+G (2d, p) and CBS-QB3 level.


Figure 3.9 Potential energy barriers for internal rotations of the $\mathrm{CS}-\mathrm{CC}$ bond in $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}$ 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.


Figure 3.10 Potential energy barriers for internal rotations of the QCS-CC
$\left(\mathrm{HOOCH}_{2} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$ bonds in QCS-CC $\left(\mathrm{HOOCH}_{2} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$, jQCS-CC $\left(\mathrm{jOOCH}_{2} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), \mathrm{QCS}-\mathrm{CjC}\left(\mathrm{HOOCH}_{2} \mathrm{~S}-\mathrm{CHjCH}_{3}\right)$ and $\mathrm{QCS}-\mathrm{CCj}$ $\left(\mathrm{HOOCH}_{2} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{j}\right)$ at B3LYP/6-31G(d) level.


Figure 3.11 Potential energy barriers for internal rotations of the $\mathrm{CS}-\mathrm{C}(\mathrm{Q}) \mathrm{C}\left(\mathrm{CH}_{3} \mathrm{~S}-\right.$ $\left.\mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}\right)$ bonds in $\mathrm{CS}-\mathrm{C}(\mathrm{Q}) \mathrm{C}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}\right), \mathrm{CjS}-\mathrm{C}(\mathrm{Q}) \mathrm{C}\left(\mathrm{CH}_{2} \mathrm{~S}-\right.$ $\left.\mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{3}\right), \mathrm{CS}-\mathrm{C}(\mathrm{Qj}) \mathrm{C}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}(\mathrm{OOj}) \mathrm{CH}_{3}\right)$ and $\mathrm{CS}-\mathrm{C}(\mathrm{Q}) \mathrm{Cj}\left(\mathrm{CH}_{3} \mathrm{~S}-\right.$ $\left.\mathrm{CH}(\mathrm{OOH}) \mathrm{CH}_{2 \mathrm{j}}\right)$ at B3LYP/6-31G(d) level.


Figure 3.12 Potential energy barriers for internal rotations of the $\mathrm{CS}-\mathrm{CCQ}\left(\mathrm{CH}_{3} \mathrm{~S}-\right.$ $\left.\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}\right)$ bonds in $\mathrm{CS}-\mathrm{CCQ}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}\right), \mathrm{CjS}-\mathrm{CCQ}\left(\mathrm{CH}_{2} \mathrm{~S}-\right.$ $\left.\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}\right)$, $\mathrm{CS}-\mathrm{CjCQ}\left(\mathrm{CH}_{3} \mathrm{~S}-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOH}\right)$ and $\mathrm{CS}-\mathrm{CCQj}\left(\mathrm{CH}_{3} \mathrm{~S}-\right.$ $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OOj}$ ) 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.


Figure 3.13 Potential energy barriers for internal rotations of the $\mathrm{C}-\mathrm{Q}$ bonds in Q -$\mathrm{CSCC}\left(\mathrm{HOO}-\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}\right)$, $\mathrm{jQ}-\mathrm{CSCC}\left(\mathrm{jOO}-\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}\right), \mathrm{Q}-\mathrm{CSCjC}(\mathrm{HOO}-$ $\left.\mathrm{CH}_{2} \mathrm{SCHjCH}_{3}\right)$ and $\mathrm{Q}-\mathrm{CSCCj}\left(\mathrm{HOO}-\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}\right)$ at $\mathrm{B} 3 \mathrm{LYP} / 6-31 \mathrm{G}(\mathrm{d})$ level.


Figure 3.14 Potential energy barriers for internal rotations of the C--Q bonds in CSC(-Q)C $\left(\mathrm{CH}_{3} \mathrm{SCH}(-\mathrm{OOH}) \mathrm{CH}_{3}\right), \mathrm{CjSC}(-\mathrm{Q}) \mathrm{C}\left(\mathrm{CH}_{2} \mathrm{SCH}(-\mathrm{OOH}) \mathrm{CH}_{3}\right), \mathrm{CSC}(-\mathrm{Qj}) \mathrm{C}$ $\left(\mathrm{CH}_{3} \mathrm{SCH}(-\mathrm{OOj}) \mathrm{CH}_{3}\right)$ and $\mathrm{CSC}(-\mathrm{Q}) \mathrm{Cj}\left(\mathrm{CH}_{3} \mathrm{SCH}(-\mathrm{OOH}) \mathrm{CH}_{2} \mathrm{j}\right)$ at $\mathrm{B} 3 \mathrm{LYP} / 6-31 \mathrm{G}(\mathrm{d})$ level.


Figure 3.15 Potential energy barriers for internal rotations of the C--Q bonds in CSCC$\mathrm{Q}\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}-\mathrm{OOH}\right), \mathrm{CjSCC}-\mathrm{Q}\left(\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2}-\mathrm{OOH}\right), \mathrm{CSCjC}-\mathrm{Q}$ $\left(\mathrm{CH}_{3} \mathrm{SCHjCH}_{2}-\mathrm{OOH}\right)$ and $\mathrm{CSCC}-\mathrm{Qj}\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2}-\mathrm{OOj}\right)$ 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.


Figure 3.16 Potential energy barriers for internal rotations of the $\mathrm{CO}-\mathrm{OH}$ bonds in $\mathrm{HO}-$ OCSCC $\left(\mathrm{HO}-\mathrm{OCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}\right), \mathrm{HO}-\mathrm{OCSCjC}\left(\mathrm{HO}-\mathrm{OCH}_{2} \mathrm{SCHjCH}_{3}\right)$ and HO --$\mathrm{OCSCCj}\left(\mathrm{HO}-\mathrm{OCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}\right)$ at B3LYP/6-31G(d) level.

(a) $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{O}-\mathrm{OH}) \mathrm{CH}_{3}$
$\mathrm{CjSC}(\mathrm{O}-\mathrm{OH}) \mathrm{C}$

(b) $\mathrm{CH}_{2} \mathrm{SCH}(\mathrm{O}-\mathrm{OH}) \mathrm{CH}_{3}$

(c) $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{O}-\mathrm{OH}) \mathrm{CH}_{2} \mathrm{j}$

Figure 3.17 Potential energy barriers for internal rotations of the $\mathrm{CO}-\mathrm{OH}$ bonds in $\mathrm{CSC}(\mathrm{O}--\mathrm{OH}) \mathrm{C}\left(\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{O}-\mathrm{OH}) \mathrm{CH}_{3}\right), \mathrm{CjSC}(\mathrm{O}-\mathrm{OH}) \mathrm{C}\left(\mathrm{CH}_{2} \mathrm{SCH}(\mathrm{O}-\mathrm{OH}) \mathrm{CH}_{3}\right)$ and $\mathrm{CSC}(\mathrm{O}--\mathrm{OH}) \mathrm{Cj}\left(\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{O}-\mathrm{OH}) \mathrm{CH}_{2} \mathrm{j}\right)$ at B3LYP/6-31G(d) level.


Figure 3.18 Potential energy barriers for internal rotations of the $\mathrm{CO}--\mathrm{OH}$ bonds in $\mathrm{CSCCO}-\mathrm{OH}\left(\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{O}-\mathrm{OH}\right), \mathrm{CjSCCO}-\mathrm{OH}\left(\mathrm{CH}_{2} \mathrm{SCH} \mathrm{SH}_{2} \mathrm{O}-\mathrm{OH}\right)$ and $\mathrm{CSCjCO}-\mathrm{OH}\left(\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{O}-\mathrm{OH}\right)$ at B3LYP/6-31G(d) level.

Then, the internal rotor potentials optimized under the level of B3LYP/6$3 \lg (2 \mathrm{~d}, 2 \mathrm{p})$ for the targeted bonds in the stable molecules of $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ and $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ 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 $\mathrm{CS}(=\mathrm{O})-\mathrm{COH}$ bond in $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ at B3LYP/6$31 \mathrm{G}(2 \mathrm{~d}, 2 \mathrm{p})$ level.


Figure3.21 Potential energy barriers for internal rotation of the $\mathrm{CS}(=\mathrm{O})-\mathrm{C}(\mathrm{OH}) \mathrm{C}$ bond in $\mathrm{CH} 3 \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ at B3LYP/6-31G(2d,2p) level.

Figure 3.20 Potential energy barriers for internal rotation of the $\mathrm{CS}(=\mathrm{O}) \mathrm{C}--\mathrm{OH}$ bond in $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ at B3LYP/6-
$31 \mathrm{G}(2 \mathrm{~d}, 2 \mathrm{p})$ level.


Figure 3.22 Potential energy barriers for internal rotation of the $\mathrm{CS}(=\mathrm{O}) \mathrm{C}(--\mathrm{OH}) \mathrm{C}$ bond in $\mathrm{CH} 3 \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ at B3LYP/6-31G(2d,2p) level.

### 3.2.6 $\mathrm{S}^{\circ} \mathbf{2 9 8}$ and $\mathrm{Cp}^{\circ}(\mathbf{T})$

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 298 K 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 gasphase thermodynamic property vs. temperature data of each species are listed in Table B.4-B. 8 in Appendix B, with a temperature range of $1-5000 \mathrm{~K}$. All these data are also ideal gas thermodynamic properties at standard state ( $\mathrm{P}=1 \mathrm{~atm}$ and $\mathrm{T}=298 \mathrm{~K}$ ). 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 | $\mathbf{S}^{\circ}{ }_{\mathbf{2 9 8 k}}$ | $\mathbf{C p}$ <br> $\mathbf{3 0 0}$ | $\mathbf{C p}$ <br> $\mathbf{4 0 0}$ | $\mathbf{C p}$ <br> $\mathbf{5 0 0}$ | $\mathbf{C p}$ <br> $\mathbf{6 0 0}$ | $\mathbf{C p}$ <br> $\mathbf{8 0 0}$ | $\mathbf{C p}$ <br> $\mathbf{1 0 0 0}$ | $\mathbf{C p}$ <br> $\mathbf{1 5 0 0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 $\mathrm{Hf}, \mathrm{S}, \mathrm{Cp}(\mathrm{t})$, bond energies, internal rotor potentials, vibration frequencies properties and molecular structures are presented for the lowest energy conformers of parent $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ and three of its main partial oxidation intermediates with one attached hydrogen peroxide group: $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$, $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$, 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 $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and Their Radicals Formed After Losing One H Atom.

| Species | Moments <br> $(\text { Bohr })^{2}$of Inertia, units amu | Frequencies ( $\mathrm{cm}^{-1}$ ) |
| :---: | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ | $\begin{aligned} & \hline 2595.8 \\ & 65.6 \\ & 835.9 \end{aligned}$ | $\begin{aligned} & 88,116,169,265,303,492,657,707,861, \\ & 993,983,1033,1049,1187,231,1365, \\ & 1412,1448,1467,1486,1797,2897,3043, \\ & 3058,3124,3128,3136 \end{aligned}$ |
| $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO}$ | $\begin{aligned} & 226.1 \\ & 683.1 \\ & 836.6 \end{aligned}$ | 72, 114, 190, 267, 318, 388, 483, 662, 816, 849, 923, 1021, 1037, 1184, 1231, 1402, 1412, 1445, 1805, 2900, 3059, 3131, 3154, 3283 |
| $\mathrm{CH}_{3} \mathrm{SCHjCHO}$ | $\begin{aligned} & 257.1 \\ & 565.5 \\ & 811.3 \end{aligned}$ | 71, 170, 216, 294, 325, 661, 668, 709, 810, 958, 967, 1004, 1108, 1360, 1380, 1415, 1457, 1461, 1606, 2906, 3063, 3156, 3175, 3175 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}$ | $\begin{aligned} & 268.2 \\ & 626.0 \\ & 784.6 \end{aligned}$ | 89, 157, 180, 204, 265, 581, 678, 715, 765, 796, 978, 996, 1173, 1246, 1357, 1405, 1467, 1490, 1935, 3039, 3042, 3105, 3123, 3140 |
| $\mathrm{CH}_{3} \mathrm{CH} 2 \mathrm{~S} \mathrm{CHO}$ | $\begin{aligned} & 317.4 \\ & 564.0 \\ & 783.8 \end{aligned}$ | 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 |
| $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{SCHO}$ | $\begin{aligned} & \hline 316.0 \\ & 527.9 \\ & 752.7 \end{aligned}$ | 72, 200, 221, 274, 318, 512, 525, 647, 729, 768, 930, 1048, 1077, 1227, 1271, 1368, 1445, 1475, 1752, 2941, 3074, 3135, 3148, 3258 |
| $\mathrm{CH}_{3} \mathrm{CHjSCHO}$ | $\begin{aligned} & \hline 190.9 \\ & 742.9 \\ & 922.1 \end{aligned}$ | $70,91,168,263,330,445,535,687,762$, $885,1002,1030,1112,1303,1362,1412$, 1474, 1487, 1745, 2964, 2971, 3046, 3087, 3197 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}$ | $\begin{aligned} & 315.2 \\ & 556.2 \\ & 780.7 \end{aligned}$ | 65, 154, 254, 276, 349, 478, 578, 612, 767, $976,1054,1073,1274,1291,1418,1463$, $1494,1503,1842,3032,3058,3094,3105$, 3125 |
| $\mathrm{CH}_{3} \mathrm{SC}=\mathrm{OCH}_{3}$ | $\begin{aligned} & 247.4 \\ & 590.8 \\ & 815.5 \end{aligned}$ | 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 |
| $\mathrm{CH}_{2} \mathrm{SC}=\mathrm{OCH}_{3}$ | $\begin{aligned} & 234.5 \\ & 570.1 \\ & 793.5 \end{aligned}$ | $45,143,235,254,355,380,474,523,600$, 821, 922, 990, 1013, 1120, 1371, 1391, 1468, 1476, 1783, 3040, 3105, 3130, 3158, 3299 |
| $\mathrm{CH}_{3} \mathrm{SC}=\mathrm{OCH}_{2} \mathrm{j}$ | $\begin{aligned} & 242.9 \\ & 555.3 \\ & 786.8 \end{aligned}$ | 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 $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ and Their Radicals Formed After Losing One H Atom.

| Species | Moments of Inertia, units amu (Bohr) ${ }^{2}$ | Frequencies ( $\mathrm{cm}^{-1}$ ) |
| :---: | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | $\begin{aligned} & 186.5 \\ & 475.2 \\ & 578.2 \end{aligned}$ | $\begin{aligned} & \hline 90,172,208,277,350,638,709,761,960, \\ & 973,980,1063,1084,1281,1303,1360, \\ & 1413,1466,1473,1485,1495,1502,3025, \\ & 3034,3038,3078,3087,3109,3113,3126 \\ & \hline \end{aligned}$ |
| $\mathrm{CH}_{2} \mathrm{j} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | $\begin{aligned} & 166.9 \\ & 459.0 \\ & 546.7 \end{aligned}$ | $\begin{aligned} & 101,211,240,282,363,418,641,767, \\ & 828,924,976,1062,1080,1277,1301, \\ & 1404,1413,1471,1490,1502,3028,3046, \\ & 3089,3093,3115,3139,3265 \end{aligned}$ |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ | $\begin{aligned} & 183.3 \\ & 424.5 \\ & 573.5 \end{aligned}$ | 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 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ | $\begin{gathered} 186.1 \\ 444.2 \\ 550.8 \end{gathered}$ | $\begin{aligned} & 95,166,207,258,319,546,626,702,761, \\ & 953,974,1063,1071,1224,1264,1356, \\ & 1454,1469,1480,1486,3035,3046,3098, \\ & 3115,3128,3142,3245 \end{aligned}$ |
| $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | $\begin{aligned} & 265.4 \\ & 1412.5 \\ & 1575.6 \end{aligned}$ | 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 |
| $\mathrm{jOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ | $\begin{aligned} & \hline 277.3 \\ & 1330.9 \\ & 1510.1 \end{aligned}$ | $\begin{aligned} & 15,57,108,199,241,274,351,453,656, \\ & 776,797,864,914,990,1050,1079,1159, \\ & 1219,1269,1298,1323,1419,1453,1490, \\ & 1496,1506,3034,3047,3069,3092,3100, \\ & 3115,3138 \end{aligned}$ |
| $\mathrm{HOOCH}_{2} \mathrm{SCHjCH}_{3}$ | $\begin{aligned} & 253.1 \\ & 1410.4 \\ & 1567.3 \end{aligned}$ | $50,68,100,122,188,216,260,329,396$, $444,719,773,873,953,1006,1012,1037$, $1110,1223,1298,1321,1363,1412,1473$, $1488,1493,2959,3027,3041,3082,3084$, 3167,3777 |
| $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ | $\begin{aligned} & \hline 473.1 \\ & 820.3 \\ & 1160.9 \end{aligned}$ | 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 |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ | $\begin{aligned} & \hline 422.0 \\ & 924.4 \\ & 1240.4 \end{aligned}$ | $89,120,136,196,208,249,268,333,408$, $475,698,730,857,881,974,978,1033$, $1090,1119,1271,1344,1354,1368,1404$, $1466,1486,1490,1499,3040,3045,3047$, $3113,3117,3127,3148,3781$ |
| $\mathrm{CH}_{2} \mathrm{jSCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ | $\begin{aligned} & 395.6 \\ & 905.9 \\ & 1214.1 \end{aligned}$ | $\begin{aligned} & 82,124,198,203,239,257,270,340,405, \\ & 454,478,714,817,861,889,936,1030, \\ & 1088,1119,1265,1348,1372,1396,1405, \\ & 1486,1499,3041,3064,3114,3118,3152, \\ & 3280,3781 \end{aligned}$ |

Table A. 2 Frequencies and Moments of Inertia From CBS-QB3 Output Files of Stable $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}, \mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ and Their Radicals Formed After Losing One H Atom. (Continued)

| Species | Moments of Inertia, units amu (Bohr) ${ }^{2}$ | Frequencies ( $\mathrm{cm}^{-1}$ ) |
| :---: | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOj}) \mathrm{CH}_{3}$ | $\begin{aligned} & 429.0 \\ & 871.1 \\ & 1198.3 \end{aligned}$ | $61,98,145,184,230,287,331,435,454$, $698,727,802,974,979,1007,1082,1109$, $1169,1281,1336,1359,1409,1468,1486$, $1488,1495,3045,3045,3087,3122,3123$, 3130,3143 |
| $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2} \mathrm{j}$ | $\begin{aligned} & 407.2 \\ & 920.4 \\ & 1217.7 \end{aligned}$ | $83,116,137,187,201,228,265,318,400$, $481,553,692,758,861,879,974,974$, $1050,1108,1216,1346,1349,1358,1447$, $1465,1488,3045,3049,3127,3145,3148$, 3259,3764 |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ | $\begin{aligned} & \hline 144.6 \\ & 1850.4 \\ & 1960.7 \end{aligned}$ | $-109,38,80,116,121,185,247,318,464$, 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 |
| $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ | $\begin{aligned} & 129.9 \\ & 1806.3 \\ & 1907.5 \end{aligned}$ | $442,78,116,129,191,211,272,317,385$, 478, 744, 811, 832, 930, 941, 1023, 1034, 1087, 1211, 1264, 1286, 1368, 1401, 1408, 1492, 1531, 3012, 3056, 3062, 3116, 3148, 3275, 3769 |
| $\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{OOH}$ | $\begin{aligned} & 249.7 \\ & 1441.7 \\ & 1522.9 \end{aligned}$ | $\begin{aligned} & 47,59,129,162,193,217,268,418,449, \\ & 598,695,755,844,942,968,974,1032, \\ & 1121,1257,1327,1354,1362,1369,1457, \\ & 1468,1482,3014,3044,3070,3128,3139, \\ & 3186,3774 \end{aligned}$ |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOj}$ | $\begin{aligned} & \hline 139.7 \\ & 1799.7 \\ & 1905.0 \end{aligned}$ | $40,70,92,123,185,258,313,508,702$, $761,798,945,970,981,1015,1090,1185$, $1186,1266,1292,1360,1392,1469,1483$, $1495,1504,3037,3043,3064,3090,3116$, 3124,3132 |

Table A. 3 Frequencies and Moments of Inertia From CBS-QB3 Output Files of Stable $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}, \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$.

| Species | Moments of Inertia, units amu $(\mathrm{Bohr})^{2}$ | Frequencies $\left(\mathrm{cm}^{-1}\right)$ |
| :--- | :--- | :--- |
| $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$ | 106.1 | $-119,111,164,203,372,703$, |
|  | 553.1 | $727,952,981,988,1079,1214$, |
|  | 636.1 | $1221,1356,1401,1468,1485$, |
|  |  | $1519,2970,3010,3029,3100$, |
|  |  | 3128,3834 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}$ | 307.1 | $65,130,193,259,337,347$, |
|  | 722.6 | $458,636,682,762,921,977$, |
|  | 859.5 | $1043,1066,1073,1190,1284$, |
|  |  | $1295,1331,1396,1414,1476$, |
|  |  | $1487,1496,1499,3017,3025$, |
|  |  | $3057,3086,3093,3110,3116$, |
|  |  | 3799 |
|  |  | $109,185,214,283,308,366$, |
|  |  | 373.6 |
|  | 769.3 | $381,632,706,880,937,991$, |
|  |  | $1065,1080,1150,1299,1327$, |
|  |  | $1380,1454,1468,1489,3034$, |
|  |  | $3037,3117,3137,3148,3826$ |
| $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3} \mathrm{OH}$ | 429.0 | $95,201,212,246,278,292,$, |
|  | 816.1 | $350,454,506,592,635,662$, |
|  | 853.7 | $902,940,953,1015,1028$, |
|  |  | $1112,1148,1204,1325,1353$, |
|  |  | $1410,1453,1456,1470,1490$, |
|  |  | $1496,3031,3040,3069,3104$, |
|  |  | $3108,3138,3152,3493$ |

## 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 ${ }^{\text {a }}$ of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ and its Radicals.

| (a) $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ |  |  |  | (b) $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CHO}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  | T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  |
|  | /mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) |  | /mol/K) | $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ | ( $\mathrm{kcal} / \mathrm{mol}$ ) |
| 1.00 | 7.949 | 18.405 | . 008 | 1.00 | 7.949 | 19.066 | . 008 |
| 50.00 | 10.444 | 50.512 | . 436 | 50.00 | 10.556 | 51.416 | . 443 |
| 100.00 | 13.794 | 58.849 | 1.047 | 100.00 | 13.909 | 59.782 | 1.056 |
| 150.00 | 16.192 | 64.907 | 1.799 | 150.00 | 16.726 | 65.964 | 1.824 |
| 200.00 | 18.403 | 69.861 | 2.664 | 200.00 | 19.208 | 71.113 | 2.724 |
| 250.00 | 20.740 | 74.209 | 3.642 | 250.00 | 21.602 | 75.651 | 3.744 |
| 298.00 | 23.103 | 78.046 | 4.694 | 298.00 | 23.856 | 79.632 | 4.835 |
| 300.00 | 23.203 | 78.201 | 4.740 | 300.00 | 23.949 | 79.792 | 4.883 |
| 400.00 | 28.090 | 85.540 | 7.307 | 400.00 | 28.293 | 87.279 | 7.500 |
| 500.00 | 32.440 | 92.277 | 10.339 | 500.00 | 31.954 | 93.990 | 10.518 |
| 600.00 | 36.120 | 98.517 | 13.773 | 600.00 | 34.962 | 100.082 | 13.869 |
| 700.00 | 39.221 | 104.316 | 17.544 | 700.00 | 37.461 | 105.659 | 17.494 |
| 800.00 | 41.861 | 109.723 | 21.602 | 800.00 | 39.575 | 110.797 | 21.348 |
| 900.00 | 44.128 | 114.782 | 25.904 | 900.00 | 41.388 | 115.561 | 25.399 |
| 1000.00 | 46.084 | 119.530 | 30.417 | 1000.00 | 42.955 | 120.001 | 29.618 |
| 1100.00 | 47.777 | 123.999 | 35.112 | 1100.00 | 44.316 | 124.156 | 33.983 |
| 1200.00 | 49.245 | 128.217 | 39.965 | 1200.00 | 45.499 | 128.061 | 38.475 |
| 1300.00 | 50.519 | 132.207 | 44.954 | 1300.00 | 46.529 | 131.742 | 43.078 |
| 1400.00 | 51.627 | 135.989 | 50.063 | 1400.00 | 47.428 | 135.222 | 47.777 |
| 1500.00 | 52.594 | 139.582 | 55.275 | 1500.00 | 48.214 | 138.519 | 52.560 |
| 2000.00 | 55.915 | 155.209 | 82.489 | 2000.00 | 50.931 | 152.795 | 77.416 |
| 2500.00 | 57.743 | 167.897 | 110.946 | 2500.00 | 52.437 | 164.333 | 103.292 |
| 3000.00 | 58.832 | 178.526 | 140.111 | 3000.00 | 53.337 | 173.977 | 129.754 |
| 3500.00 | 59.525 | 187.649 | 169.713 | 3500.00 | 53.912 | 182.244 | 156.576 |
| 4000.00 | 59.990 | 195.628 | 199.599 | 4000.00 | 54.298 | 189.469 | 183.635 |
| 4500.00 | 60.317 | 202.713 | 229.680 | 4500.00 | 54.570 | 195.880 | 210.856 |
| 5000.00 | 60.554 | 209.080 | 259.901 | 5000.00 | 54.767 | 201.640 | 238.193 |
| Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=52.5$ |  |  |  | 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 ${ }^{\text {a }}$ of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CHO}$ and its Radicals. (Continued)

| (c) $\mathrm{CH}_{3} \mathrm{SCHjCHO}$ |  |  |  | (d) $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CjO}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})]$ |  | T( | Cp | S | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |
|  | mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) |  | /mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | (kcal/mol) |
| 1.00 | 7.949 | 18.170 | . 008 | 1.00 | 7.949 | 18.279 | . 008 |
| 50.00 | 9.938 | 50.274 | . 433 | 50.00 | 10.140 | 50.192 | . 429 |
| 100.00 | 12.936 | 58.091 | 1.006 | 100.00 | 13.920 | 58.472 | 1.038 |
| 150.00 | 15.360 | 63.804 | 1.716 | 150.00 | 16.306 | 64.584 | 1.796 |
| 200.00 | 17.609 | 68.524 | 2.540 | 200.00 | 18.478 | 69.565 | 2.665 |
| 250.00 | 19.940 | 72.696 | 3.478 | 250.00 | 20.742 | 73.924 | 3.645 |
| 298.00 | 22.224 | 76.387 | 4.490 | 298.00 | 22.947 | 77.749 | 4.694 |
| 300.00 | 22.318 | 76.535 | 4.534 | 300.00 | 23.038 | 77.903 | 4.740 |
| 400.00 | 26.860 | 83.578 | 6.997 | 400.00 | 27.372 | 85.125 | 7.265 |
| 500.00 | 30.772 | 89.995 | 9.885 | 500.00 | 31.090 | 91.635 | 10.193 |
| 600.00 | 34.011 | 95.892 | 13.129 | 600.00 | 34.185 | 97.577 | 13.462 |
| 700.00 | 36.699 | 101.336 | 16.669 | 700.00 | 36.780 | 103.041 | 17.014 |
| 800.00 | 38.961 | 106.383 | 20.455 | 800.00 | 38.987 | 108.094 | 20.805 |
| 900.00 | 40.889 | 111.081 | 24.450 | 900.00 | 40.884 | 112.794 | 24.801 |
| 1000.00 | 42.546 | 115.473 | 28.624 | 1000.00 | 42.523 | 117.184 | 28.973 |
| 1100.00 | 43.976 | 119.593 | 32.952 | 1100.00 | 43.945 | 121.301 | 33.298 |
| 1200.00 | 45.213 | 123.470 | 37.413 | 1200.00 | 45.179 | 125.176 | 37.756 |
| 1300.00 | 46.287 | 127.130 | 41.989 | 1300.00 | 46.252 | 128.833 | 42.329 |
| 1400.00 | 47.220 | 130.593 | 46.665 | 1400.00 | 47.186 | 132.293 | 47.002 |
| 1500.00 | 48.035 | 133.877 | 51.429 | 1500.00 | 48.002 | 135.575 | 51.762 |
| 2000.00 | 50.833 | 148.114 | 76.219 | 2000.00 | 50.810 | 149.803 | 76.538 |
| 2500.00 | 52.376 | 159.634 | 102.057 | 2500.00 | 52.361 | 161.320 | 102.367 |
| 3000.00 | 53.296 | 169.269 | 128.493 | 3000.00 | 53.285 | 170.952 | 128.797 |
| 3500.00 | 53.882 | 177.531 | 155.298 | 3500.00 | 53.874 | 179.212 | 155.597 |
| 4000.00 | 54.276 | 184.752 | 182.344 | 4000.00 | 54.269 | 186.432 | 182.638 |
| 4500.00 | 54.552 | 191.161 | 209.555 | 4500.00 | 54.547 | 192.841 | 209.846 |
| 5000.00 | 54.753 | 196.919 | 236.884 | 5000.00 | 54.749 | 198.598 | 237.173 |
| Zero Point Vibration Energy (kcal/mol) $=45.0$ |  |  |  | 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 ${ }^{\text {a }}$ of Radicals of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and Its Radicals.

| (a) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ |  |  |  | (b) $\mathrm{CH}_{2} \mathrm{jCH}_{2} \mathrm{SCHO}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Сp | S [H | )-H(0K)] | $\mathrm{T}(\mathrm{K})$ | Cp | S | )-H(0K)] |
| ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | (kcal/mol) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | (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 ( $\mathrm{kcal} / \mathrm{mol}$ ) $=53.0$ |  |  |  | Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=44.0$ |  |  |  |

Table B. 2 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of Radicals of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCHO}$ and Its Radicals. (Continued)

| (c) $\mathrm{CH}_{3} \mathrm{CHjSCHO}$ |  |  |  | (d) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCjO}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  | T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  |
|  | /mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) |  | /mol/K) | $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ | ( $\mathrm{kcal} / \mathrm{mol}$ ) |
| 1.00 | 7.949 | 18.272 | . 008 | 1.00 | 7.949 | 18.317 | . 008 |
| 50.00 | 10.991 | 50.930 | . 453 | 50.00 | 10.058 | 50.580 | . 438 |
| 100.00 | 14.032 | 59.525 | 1.082 | 100.00 | 12.980 | 58.430 | 1.013 |
| 150.00 | 16.544 | 65.693 | 1.848 | 150.00 | 15.743 | 64.219 | 1.732 |
| 200.00 | 18.868 | 70.767 | 2.734 | 200.00 | 18.218 | 69.086 | 2.582 |
| 250.00 | 21.146 | 75.216 | 3.734 | 250.00 | 20.530 | 73.396 | 3.552 |
| 298.00 | 23.307 | 79.109 | 4.801 | 298.00 | 22.670 | 77.179 | 4.589 |
| 300.00 | 23.396 | 79.265 | 4.848 | 300.00 | 22.758 | 77.331 | 4.634 |
| 400.00 | 27.643 | 86.577 | 7.404 | 400.00 | 26.952 | 84.451 | 7.123 |
| 500.00 | 31.323 | 93.143 | 10.357 | 500.00 | 30.635 | 90.862 | 10.007 |
| 600.00 | 34.410 | 99.127 | 13.648 | 600.00 | 33.762 | 96.724 | 13.231 |
| 700.00 | 37.005 | 104.625 | 17.223 | 700.00 | 36.412 | 102.126 | 16.744 |
| 800.00 | 39.212 | 109.709 | 21.037 | 800.00 | 38.675 | 107.134 | 20.501 |
| 900.00 | 41.105 | 114.434 | 25.055 | 900.00 | 40.621 | 111.799 | 24.468 |
| 1000.00 | 42.737 | 118.847 | 29.249 | 1000.00 | 42.302 | 116.164 | 28.616 |
| 1100.00 | 44.150 | 122.985 | 33.595 | 1100.00 | 43.757 | 120.262 | 32.921 |
| 1200.00 | 45.373 | 126.877 | 38.072 | 1200.00 | 45.019 | 124.121 | 37.361 |
| 1300.00 | 46.434 | 130.549 | 42.664 | 1300.00 | 46.115 | 127.766 | 41.919 |
| 1400.00 | 47.357 | 134.022 | 47.355 | 1400.00 | 47.068 | 131.217 | 46.580 |
| 1500.00 | 48.162 | 137.315 | 52.132 | 1500.00 | 47.899 | 134.491 | 51.329 |
| 2000.00 | 50.923 | 151.584 | 76.975 | 2000.00 | 50.753 | 148.697 | 76.067 |
| 2500.00 | 52.441 | 163.121 | 102.851 | 2500.00 | 52.325 | 160.203 | 101.872 |
| 3000.00 | 53.344 | 172.767 | 129.316 | 3000.00 | 53.260 | 169.830 | 128.287 |
| 3500.00 | 53.919 | 181.034 | 156.141 | 3500.00 | 53.856 | 178.087 | 155.077 |
| 4000.00 | 54.305 | 188.260 | 183.203 | 4000.00 | 54.256 | 185.305 | 182.111 |
| 4500.00 | 54.576 | 194.672 | 210.427 | 4500.00 | 54.536 | 191.712 | 209.313 |
| 5000.00 | 54.772 | 200.432 | 237.767 | 5000.00 | 54.740 | 197.468 | 236.635 |
| Zero Point Vibration Energy (kcal/mol) $=44.1$ |  |  |  | Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=45.3$ |  |  |  |

${ }^{3}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm.

Table B3 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of Radicals of $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and Its Radicals.

| (a) $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ |  |  |  | (b) $\mathrm{CH}_{2} \mathrm{j} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | S | T)-H(0K)] | T(K) | Cp | S | )-H(0K)] |
| ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) | $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ |  | $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ | (kcal/mol) |
| 1.00 | 7.949 | 16.035 | . 008 | 1.00 | 7.949 | 16.687 | . 008 |
| 50.00 | 12.416 | 51.666 | . 524 | 50.00 | 10.441 | 49.595 | . 454 |
| 100.00 | 14.779 | 61.021 | 1.206 | 100.00 | 13.598 | 57.757 | 1.053 |
| 150.00 | 16.971 | 67.420 | 2.000 | 150.00 | 16.814 | 63.881 | 1.814 |
| 200.00 | 19.242 | 72.605 | 2.905 | 200.00 | 19.669 | 69.110 | 2.728 |
| 250.00 | 21.602 | 77.145 | 3.926 | 250.00 | 22.242 | 73.773 | 3.777 |
| 298.00 | 23.916 | 81.130 | 5.018 | 298.00 | 24.527 | 77.870 | 4.900 |
| 300.00 | 24.012 | 81.290 | 5.066 | 300.00 | 24.619 | 78.035 | 4.949 |
| 400.00 | 28.702 | 88.837 | 7.705 | 400.00 | 28.840 | 85.701 | 7.628 |
| 500.00 | 32.864 | 95.689 | 10.788 | 500.00 | 32.344 | 92.517 | 10.693 |
| 600.00 | 36.399 | 101.993 | 14.256 | 600.00 | 35.225 | 98.669 | 14.076 |
| 700.00 | 39.395 | 107.828 | 18.050 | 700.00 | 37.628 | 104.279 | 17.722 |
| 800.00 | 41.958 | 113.253 | 22.121 | 800.00 | 39.674 | 109.435 | 21.590 |
| 900.00 | 44.169 | 118.320 | 26.430 | 900.00 | 41.438 | 114.208 | 25.647 |
| 1000.00 | 46.087 | 123.070 | 30.945 | 1000.00 | 42.971 | 118.651 | 29.870 |
| 1100.00 | 47.753 | 127.539 | 35.639 | 1100.00 | 44.308 | 122.807 | 34.235 |
| 1200.00 | 49.203 | 131.754 | 40.488 | 1200.00 | 45.475 | 126.711 | 38.726 |
| 1300.00 | 50.466 | 135.740 | 45.473 | 1300.00 | 46.495 | 130.389 | 43.325 |
| 1400.00 | 51.568 | 139.518 | 50.576 | 1400.00 | 47.387 | 133.866 | 48.020 |
| 1500.00 | 52.531 | 143.107 | 55.782 | 1500.00 | 48.170 | 137.161 | 52.799 |
| 2000.00 | 55.855 | 158.715 | 82.965 | 2000.00 | 50.886 | 151.423 | 77.632 |
| 2500.00 | 57.695 | 171.391 | 111.394 | 2500.00 | 52.401 | 162.952 | 103.488 |
| 3000.00 | 58.795 | 182.012 | 140.539 | 3000.00 | 53.309 | 172.590 | 129.934 |
| 3500.00 | 59.495 | 191.130 | 170.123 | 3500.00 | 53.889 | 180.853 | 156.743 |
| 4000.00 | 59.967 | 199.106 | 199.996 | 4000.00 | 54.280 | 188.075 | 183.792 |
| 4500.00 | 60.298 | 206.188 | 230.067 | 4500.00 | 54.555 | 194.484 | 211.005 |
| 5000.00 | 60.538 | 212.554 | 260.279 | 5000.00 | 54.755 | 200.243 | 238.335 |
| Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=52.2$ |  |  |  | Zero Point Vibration Energy (kcal/mol) $=43.6$ |  |  |  |

${ }^{3}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm.

Table B3 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of Radicals of $\mathrm{CH}_{3} \mathrm{SC}(=\mathrm{O}) \mathrm{CH}_{3}$ and Its Radicals. (Continued)

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm.

Table B4 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ and Its Radicals.

| (a) $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ |  |  |  | (b) $\mathrm{CH}_{2} \mathrm{j} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | S [H | T)-H(0K)] | T(K) | Cp | $\mathrm{S} \quad[\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})]$ |  |
| $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) |
| 1.00 | 7.949 | 14.689 | . 008 | 1.00 | 7.949 | 15.254 | . 008 |
| 50.00 | 9.694 | 46.474 | . 423 | 50.00 | 9.286 | 46.843 | . 416 |
| 100.00 | 12.863 | 54.194 | . 990 | 100.00 | 12.479 | 54.227 | . 959 |
| 150.00 | 15.235 | 59.872 | 1.695 | 150.00 | 15.362 | 59.845 | 1.657 |
| 200.00 | 17.383 | 64.541 | 2.510 | 200.00 | 17.864 | 64.604 | 2.489 |
| 250.00 | 19.714 | 68.660 | 3.437 | 250.00 | 20.312 | 68.847 | 3.443 |
| 298.00 | 22.154 | 72.322 | 4.441 | 298.00 | 22.687 | 72.610 | 4.475 |
| 300.00 | 22.259 | 72.470 | 4.485 | 300.00 | 22.785 | 72.762 | 4.520 |
| 400.00 | 27.515 | 79.582 | 6.975 | 400.00 | 27.562 | 79.969 | 7.041 |
| 500.00 | 32.351 | 86.241 | 9.973 | 500.00 | 31.751 | 86.571 | 10.013 |
| 600.00 | 36.526 | 92.507 | 13.423 | 600.00 | 35.281 | 92.672 | 13.369 |
| 700.00 | 40.103 | 98.404 | 17.259 | 700.00 | 38.273 | 98.334 | 17.051 |
| 800.00 | 43.194 | 103.958 | 21.427 | 800.00 | 40.850 | 103.610 | 21.010 |
| 900.00 | 45.883 | 109.197 | 25.884 | 900.00 | 43.095 | 108.548 | 25.210 |
| 1000.00 | 48.231 | 114.150 | 30.593 | 1000.00 | 45.060 | 113.187 | 29.620 |
| 1100.00 | 50.282 | 118.840 | 35.521 | 1100.00 | 46.783 | 117.560 | 34.214 |
| 1200.00 | 52.074 | 123.289 | 40.640 | 1200.00 | 48.295 | 121.693 | 38.970 |
| 1300.00 | 53.639 | 127.516 | 45.928 | 1300.00 | 49.620 | 125.609 | 43.867 |
| 1400.00 | 55.008 | 131.539 | 51.362 | 1400.00 | 50.782 | 129.327 | 48.888 |
| 1500.00 | 56.207 | 135.373 | 56.924 | 1500.00 | 51.802 | 132.863 | 54.018 |
| 2000.00 | 60.357 | 152.162 | 86.172 | 2000.00 | 55.357 | 148.295 | 80.899 |
| 2500.00 | 62.662 | 165.895 | 116.979 | 2500.00 | 57.345 | 160.876 | 109.119 |
| 3000.00 | 64.040 | 177.448 | 148.681 | 3000.00 | 58.537 | 171.442 | 138.113 |
| 3500.00 | 64.919 | 187.388 | 180.936 | 3500.00 | 59.300 | 180.525 | 167.586 |
| 4000.00 | 65.510 | 196.096 | 213.553 | 4000.00 | 59.814 | 188.478 | 197.372 |
| 4500.00 | 65.925 | 203.836 | 246.418 | 4500.00 | 60.175 | 195.544 | 227.374 |
| 5000.00 | 66.228 | 210.798 | 279.460 | 5000.00 | 60.438 | 201.898 | 257.531 |
| Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=64.0$ |  |  |  | Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=55.4$ |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

Table B4 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\mathrm{a}}$ of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ and Its Radicals. (Continued)

| (c) $\mathrm{CH}_{3} \mathrm{SCHjCH}_{3}$ |  |  |  | (d) $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | $\mathrm{S} \quad[\mathrm{H}$ | T)-H(0K)] | T(K) | Cp | $\mathrm{S} \quad[\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})]$ |  |
| (cal/mol/K) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ | ( $\mathrm{kcal} / \mathrm{mol}$ ) |
| 1.00 | 7.949 | 14.511 | . 008 | 1.00 | 7.949 | 15.337 | . 008 |
| 50.00 | 9.905 | 46.337 | . 425 | 50.00 | 9.711 | 47.089 | . 423 |
| 100.00 | 13.303 | 54.295 | 1.010 | 100.00 | 13.129 | 54.900 | . 997 |
| 150.00 | 15.815 | 60.177 | 1.740 | 150.00 | 15.753 | 60.731 | 1.721 |
| 200.00 | 18.012 | 65.024 | 2.586 | 200.00 | 18.134 | 65.583 | 2.568 |
| 250.00 | 20.242 | 69.275 | 3.542 | 250.00 | 20.562 | 69.882 | 3.535 |
| 298.00 | 22.474 | 73.014 | 4.567 | 298.00 | 22.944 | 73.690 | 4.579 |
| 300.00 | 22.568 | 73.164 | 4.612 | 300.00 | 23.043 | 73.844 | 4.625 |
| 400.00 | 27.211 | 80.286 | 7.103 | 400.00 | 27.829 | 81.127 | 7.173 |
| 500.00 | 31.389 | 86.807 | 10.038 | 500.00 | 32.000 | 87.787 | 10.170 |
| 600.00 | 34.962 | 92.846 | 13.361 | 600.00 | 35.500 | 93.931 | 13.550 |
| 700.00 | 38.013 | 98.462 | 17.013 | 700.00 | 38.458 | 99.624 | 17.252 |
| 800.00 | 40.648 | 103.708 | 20.950 | 800.00 | 41.005 | 104.923 | 21.228 |
| 900.00 | 42.943 | 108.625 | 25.132 | 900.00 | 43.223 | 109.878 | 25.442 |
| 1000.00 | 44.950 | 113.250 | 29.529 | 1000.00 | 45.167 | 114.529 | 29.863 |
| 1100.00 | 46.705 | 117.614 | 34.113 | 1100.00 | 46.873 | 118.912 | 34.467 |
| 1200.00 | 48.241 | 121.742 | 38.862 | 1200.00 | 48.370 | 123.052 | 39.231 |
| 1300.00 | 49.585 | 125.654 | 43.755 | 1300.00 | 49.684 | 126.973 | 44.135 |
| 1400.00 | 50.761 | 129.369 | 48.774 | 1400.00 | 50.837 | 130.695 | 49.163 |
| 1500.00 | 51.792 | 132.905 | 53.903 | 1500.00 | 51.850 | 134.235 | 54.298 |
| 2000.00 | 55.369 | 148.338 | 80.785 | 2000.00 | 55.383 | 149.678 | 81.196 |
| 2500.00 | 57.359 | 160.922 | 109.012 | 2500.00 | 57.360 | 162.263 | 109.426 |
| 3000.00 | 58.551 | 171.491 | 138.013 | 3000.00 | 58.548 | 172.832 | 138.427 |
| 3500.00 | 59.312 | 180.575 | 167.492 | 3500.00 | 59.308 | 181.916 | 167.904 |
| 4000.00 | 59.823 | 188.530 | 197.284 | 4000.00 | 59.820 | 189.870 | 197.693 |
| 4500.00 | 60.183 | 195.597 | 227.291 | 4500.00 | 60.179 | 196.936 | 227.698 |
| 5000.00 | 60.445 | 201.951 | 257.451 | 5000.00 | 60.441 | 203.291 | 257.857 |
| Zero Point Vibration Energy (kcal/mol) = 55.4 |  |  |  | Zero Point Vibration Energy (kcal/mol) = 55.1 |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

Table B5 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ and Its Radicals.

| (a) $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ |  |  |  | (b) $\mathrm{jOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | $\mathrm{Cp}$ | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  | T(K) | Cp | [ $\mathrm{H}(\mathrm{T}) \mathrm{-H}(0 \mathrm{~K})$ ] |  |
| (cal/mol/K) |  | $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ | ( $\mathrm{kcal} / \mathrm{mol}$ ) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | (kcal/mol) |
| 1.00 | 7.949 | 20.351 | . 008 | 1.00 | 7.949 | 20.265 | . 008 |
| 50.00 | 12.292 | 54.095 | . 486 | 50.00 | 12.818 | 56.765 | . 535 |
| 100.00 | 17.212 | 64.167 | 1.228 | 100.00 | 16.390 | 66.759 | 1.266 |
| 150.00 | 20.794 | 71.853 | 2.183 | 150.00 | 19.327 | 73.972 | 2.162 |
| 200.00 | 23.756 | 78.237 | 3.297 | 200.00 | 22.010 | 79.892 | 3.195 |
| 250.00 | 26.766 | 83.850 | 4.559 | 250.00 | 24.844 | 85.096 | 4.366 |
| 298.00 | 29.806 | 88.801 | 5.917 | 298.00 | 27.733 | 89.697 | 5.627 |
| 300.00 | 29.934 | 89.000 | 5.976 | 300.00 | 27.855 | 89.882 | 5.683 |
| 400.00 | 36.260 | 98.471 | 9.289 | 400.00 | 33.866 | 98.712 | 8.772 |
| 500.00 | 41.883 | 107.169 | 13.204 | 500.00 | 39.191 | 106.844 | 12.432 |
| 600.00 | 46.598 | 115.222 | 17.635 | 600.00 | 43.641 | 114.384 | 16.580 |
| 700.00 | 50.537 | 122.700 | 22.498 | 700.00 | 47.347 | 121.388 | 21.135 |
| 800.00 | 53.873 | 129.663 | 27.723 | 800.00 | 50.470 | 127.912 | 26.030 |
| 900.00 | 56.733 | 136.170 | 33.257 | 900.00 | 53.135 | 134.007 | 31.214 |
| 1000.00 | 59.206 | 142.272 | 39.057 | 1000.00 | 55.425 | 139.721 | 36.645 |
| 1100.00 | 61.354 | 148.013 | 45.087 | 1100.00 | 57.402 | 145.093 | 42.289 |
| 1200.00 | 63.224 | 153.429 | 51.318 | 1200.00 | 59.114 | 150.159 | 48.116 |
| 1300.00 | 64.856 | 158.551 | 57.724 | 1300.00 | 60.599 | 154.947 | 54.104 |
| 1400.00 | 66.282 | 163.407 | 64.282 | 1400.00 | 61.890 | 159.482 | 60.230 |
| 1500.00 | 67.531 | 168.020 | 70.974 | 1500.00 | 63.016 | 163.789 | 66.476 |
| 2000.00 | 71.868 | 188.094 | 105.935 | 2000.00 | 66.886 | 182.496 | 99.053 |
| 2500.00 | 74.290 | 204.409 | 142.529 | 2500.00 | 69.018 | 197.666 | 133.078 |
| 3000.00 | 75.744 | 218.089 | 180.066 | 3000.00 | 70.289 | 210.368 | 167.931 |
| 3500.00 | 76.674 | 229.837 | 218.187 | 3500.00 | 71.098 | 221.266 | 203.292 |
| 4000.00 | 77.301 | 240.118 | 256.690 | 4000.00 | 71.642 | 230.796 | 238.985 |
| 4500.00 | 77.742 | 249.248 | 295.457 | 4500.00 | 72.023 | 239.257 | 274.906 |
| 5000.00 | 78.063 | 257.456 | 334.412 | 5000.00 | 72.300 | 246.860 | 310.991 |
| Zero Point Vibration Energy (kcal/mol) $=69.0$ |  |  |  | Zero Point Vibration Energy (kcal/mol) $=61.7$ |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

Table B5 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{3}$ and Its Radicals. (Continued)

| (c) $\mathrm{HOOCH}_{2} \mathrm{SCHjCH}_{3}$ |  |  |  | (d) $\mathrm{HOOCH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{j}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | S [H | T)-H(0K)] | T(K) | Cp | $\mathrm{S} \quad[\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})]$ |  |
| ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) |
| 1.00 | 7.949 | 20.269 | . 008 | 1.00 | 7.949 | 20.860 | . 008 |
| 50.00 | 13.397 | 54.539 | . 506 | 50.00 | 11.700 | 54.101 | . 471 |
| 100.00 | 18.433 | 65.467 | 1.309 | 100.00 | 16.150 | 63.577 | 1.168 |
| 150.00 | 21.958 | 73.635 | 2.324 | 150.00 | 20.145 | 70.889 | 2.078 |
| 200.00 | 24.837 | 80.345 | 3.495 | 200.00 | 23.723 | 77.172 | 3.175 |
| 250.00 | 27.651 | 86.181 | 4.807 | 250.00 | 27.125 | 82.824 | 4.447 |
| 298.00 | 30.418 | 91.266 | 6.200 | 298.00 | 30.287 | 87.851 | 5.825 |
| 300.00 | 30.534 | 91.469 | 6.261 | 300.00 | 30.416 | 88.054 | 5.886 |
| 400.00 | 36.158 | 101.020 | 9.599 | 400.00 | 36.453 | 97.637 | 9.237 |
| 500.00 | 41.074 | 109.620 | 13.468 | 500.00 | 41.483 | 106.317 | 13.142 |
| 600.00 | 45.157 | 117.470 | 17.786 | 600.00 | 45.553 | 114.243 | 17.501 |
| 700.00 | 48.553 | 124.685 | 22.477 | 700.00 | 48.888 | 121.515 | 22.229 |
| 800.00 | 51.421 | 131.353 | 27.479 | 800.00 | 51.686 | 128.223 | 27.261 |
| 900.00 | 53.879 | 137.549 | 32.747 | 900.00 | 54.080 | 134.446 | 32.552 |
| 1000.00 | 56.004 | 143.333 | 38.244 | 1000.00 | 56.152 | 140.249 | 38.066 |
| 1100.00 | 57.851 | 148.754 | 43.939 | 1100.00 | 57.957 | 145.682 | 43.774 |
| 1200.00 | 59.460 | 153.855 | 49.806 | 1200.00 | 59.534 | 150.790 | 49.650 |
| 1300.00 | 60.865 | 158.667 | 55.824 | 1300.00 | 60.914 | 155.608 | 55.674 |
| 1400.00 | 62.094 | 163.220 | 61.973 | 1400.00 | 62.125 | 160.164 | 61.827 |
| 1500.00 | 63.171 | 167.539 | 68.238 | 1500.00 | 63.189 | 164.485 | 68.094 |
| 2000.00 | 66.918 | 186.271 | 100.855 | 2000.00 | 66.907 | 183.216 | 100.712 |
| 2500.00 | 69.014 | 201.444 | 134.885 | 2500.00 | 68.999 | 198.386 | 134.735 |
| 3000.00 | 70.275 | 214.144 | 169.733 | 3000.00 | 70.260 | 211.083 | 169.574 |
| 3500.00 | 71.082 | 225.039 | 205.086 | 3500.00 | 71.069 | 221.977 | 204.921 |
| 4000.00 | 71.626 | 234.567 | 240.771 | 4000.00 | 71.616 | 231.503 | 240.600 |
| 4500.00 | 72.009 | 243.026 | 276.685 | 4500.00 | 72.000 | 239.961 | 276.510 |
| 5000.00 | 72.288 | 250.627 | 312.763 | 5000.00 | 72.281 | 247.562 | 312.583 |
| Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=60.1$ |  |  |  | Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=60.32$ |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

Table B6 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and Its Radicals.

| (a) $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ |  |  |  | (b) $\mathrm{CH}_{2} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T (K) | Cp | S [H(T)-H(0K)] |  | T(K) |  | S [H | T)-H(0K)] |
|  | /mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | (kcal/mol) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | (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) $=60.0$ |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

Table B6 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{3}$ and Its Radicals. (Continued)

| (c) $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOj}) \mathrm{CH}_{3}$ |  |  |  | (d) $\mathrm{CH}_{3} \mathrm{SCH}(\mathrm{OOH}) \mathrm{CH}_{2} \mathrm{j}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) |  | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  | T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})]$ |  |
|  | mol/K) | $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ | (kcal/mol) |  | /mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | (kcal/mol) |
| 1.00 | 7.949 | 17.865 | . 008 | 1.00 | 7.949 | 18.690 | . 008 |
| 50.00 | 11.574 | 50.797 | . 462 | 50.00 | 11.355 | 51.092 | . 447 |
| 100.00 | 16.163 | 60.279 | 1.160 | 100.00 | 17.256 | 60.851 | 1.169 |
| 150.00 | 19.698 | 67.520 | 2.060 | 150.00 | 21.548 | 68.690 | 2.144 |
| 200.00 | 22.717 | 73.598 | 3.122 | 200.00 | 25.076 | 75.372 | 3.312 |
| 250.00 | 25.678 | 78.976 | 4.331 | 250.00 | 28.372 | 81.315 | 4.648 |
| 298.00 | 28.572 | 83.725 | 5.633 | 298.00 | 31.426 | 86.553 | 6.084 |
| 300.00 | 28.693 | 83.916 | 5.691 | 300.00 | 31.551 | 86.763 | 6.147 |
| 400.00 | 34.575 | 92.972 | 8.858 | 400.00 | 37.365 | 96.642 | 9.600 |
| 500.00 | 39.746 | 101.245 | 12.581 | 500.00 | 42.199 | 105.505 | 13.587 |
| 600.00 | 44.068 | 108.875 | 16.779 | 600.00 | 46.111 | 113.547 | 18.009 |
| 700.00 | 47.674 | 115.938 | 21.371 | 700.00 | 49.324 | 120.895 | 22.786 |
| 800.00 | 50.721 | 122.500 | 26.295 | 800.00 | 52.029 | 127.656 | 27.857 |
| 900.00 | 53.328 | 128.622 | 31.500 | 900.00 | 54.351 | 133.916 | 33.179 |
| 1000.00 | 55.575 | 134.354 | 36.948 | 1000.00 | 56.368 | 139.744 | 38.717 |
| 1100.00 | 57.519 | 139.739 | 42.605 | 1100.00 | 58.130 | 145.196 | 44.444 |
| 1200.00 | 59.206 | 144.813 | 48.444 | 1200.00 | 59.673 | 150.317 | 50.336 |
| 1300.00 | 60.672 | 149.608 | 54.439 | 1300.00 | 61.028 | 155.145 | 56.372 |
| 1400.00 | 61.949 | 154.149 | 60.572 | 1400.00 | 62.218 | 159.709 | 62.536 |
| 1500.00 | 63.064 | 158.459 | 66.824 | 1500.00 | 63.266 | 164.035 | 68.811 |
| 2000.00 | 66.904 | 177.175 | 99.416 | 2000.00 | 66.940 | 182.782 | 101.455 |
| 2500.00 | 69.027 | 192.348 | 133.447 | 2500.00 | 69.016 | 197.958 | 135.490 |
| 3000.00 | 70.293 | 205.051 | 168.302 | 3000.00 | 70.270 | 210.657 | 170.335 |
| 3500.00 | 71.100 | 215.949 | 203.665 | 3500.00 | 71.075 | 221.552 | 205.686 |
| 4000.00 | 71.643 | 225.480 | 239.359 | 4000.00 | 71.620 | 231.079 | 241.368 |
| 4500.00 | 72.024 | 233.940 | 275.281 | 4500.00 | 72.003 | 239.537 | 277.279 |
| 5000.00 | 72.301 | 241.543 | 311.365 | 5000.00 | 72.283 | 247.138 | 313.354 |
| Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=61.4$ |  |  |  | Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=59.5$ |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

Table B7 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ and Its Radicals.

| (a) $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ |  |  |  | (b) $\mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | S [ H | T)-H(0K)] | T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})]$ |  |
| $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | (kcal/mol) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | (kcal/mol) |
| 1.00 | 7.949 | 20.234 | . 008 | 1.00 | 7.949 | 20.854 | . 008 |
| 50.00 | 11.267 | 52.717 | . 449 | 50.00 | 13.088 | 55.086 | . 501 |
| 100.00 | 15.336 | 61.888 | 1.124 | 100.00 | 18.259 | 65.842 | 1.293 |
| 150.00 | 17.974 | 68.623 | 1.959 | 150.00 | 21.830 | 73.950 | 2.300 |
| 200.00 | 20.382 | 74.114 | 2.918 | 200.00 | 24.752 | 80.628 | 3.465 |
| 250.00 | 23.074 | 78.938 | 4.003 | 250.00 | 27.636 | 86.452 | 4.775 |
| 298.00 | 25.937 | 83.224 | 5.178 | 298.00 | 30.470 | 91.539 | 6.169 |
| 300.00 | 26.060 | 83.398 | 5.230 | 300.00 | 30.589 | 91.743 | 6.230 |
| 400.00 | 32.220 | 91.727 | 8.146 | 400.00 | 36.304 | 101.324 | 9.579 |
| 500.00 | 37.795 | 99.516 | 11.653 | 500.00 | 41.239 | 109.959 | 13.464 |
| 600.00 | 42.503 | 106.824 | 15.675 | 600.00 | 45.299 | 117.838 | 17.798 |
| 700.00 | 46.449 | 113.671 | 20.128 | 700.00 | 48.653 | 125.072 | 22.500 |
| 800.00 | 49.795 | 120.089 | 24.945 | 800.00 | 51.479 | 131.751 | 27.511 |
| 900.00 | 52.666 | 126.116 | 30.072 | 900.00 | 53.899 | 137.951 | 32.783 |
| 1000.00 | 55.149 | 131.790 | 35.465 | 1000.00 | 55.993 | 143.736 | 38.280 |
| 1100.00 | 57.305 | 137.144 | 41.091 | 1100.00 | 57.818 | 149.155 | 43.972 |
| 1200.00 | 59.182 | 142.208 | 46.917 | 1200.00 | 59.411 | 154.252 | 49.836 |
| 1300.00 | 60.820 | 147.007 | 52.919 | 1300.00 | 60.805 | 159.060 | 55.848 |
| 1400.00 | 62.251 | 151.564 | 59.074 | 1400.00 | 62.028 | 163.609 | 61.991 |
| 1500.00 | 63.505 | 155.899 | 65.363 | 1500.00 | 63.101 | 167.923 | 68.248 |
| 2000.00 | 67.860 | 174.818 | 98.316 | 2000.00 | 66.852 | 186.634 | 100.831 |
| 2500.00 | 70.291 | 190.240 | 132.908 | 2500.00 | 68.961 | 201.794 | 134.831 |
| 3000.00 | 71.751 | 203.191 | 168.448 | 3000.00 | 70.233 | 214.485 | 169.655 |
| 3500.00 | 72.686 | 214.324 | 204.573 | 3500.00 | 71.049 | 225.375 | 204.989 |
| 4000.00 | 73.316 | 224.072 | 241.083 | 4000.00 | 71.599 | 234.899 | 240.659 |
| 4500.00 | 73.759 | 232.733 | 277.858 | 4500.00 | 71.987 | 243.355 | 276.561 |
| 5000.00 | 74.082 | 240.521 | 314.822 | 5000.00 | 72.270 | 250.954 | 312.629 |
| Zero Point Vibration Energy (kcal/mol) = 68.8 |  |  |  | Zero Point Vibration Energy (kcal/mol) $=60.3$ |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

Table B7 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\text {a }}$ of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOH}$ and Its Radicals. (Continued)

| (c) $\mathrm{CH}_{3} \mathrm{SCHjCH}_{2} \mathrm{OOH}$ |  |  |  | (d) $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{OOj}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  | T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  |
|  | /mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) |  | /mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) |
| 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) $=61.8$ |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

Table 88 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\mathrm{a}}$ of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}, \mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ and $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$.

| (a) $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$ |  |  |  | (b) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | $\mathrm{S} \quad[\mathrm{H}$ | T)-H(0K)] | T(K) | Cp | S | -H(0K)] |
| ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) |  | $(\mathrm{cal} / \mathrm{mol} / \mathrm{K})$ | ( $\mathrm{kcal} / \mathrm{mol}$ ) |
| 1.00 | 7.949 | 16.638 | . 008 | 1.00 | 7.949 | 18.751 | . 008 |
| 50.00 | 8.554 | 47.875 | . 403 | 50.00 | 10.475 | 51.154 | . 443 |
| 100.00 | 10.534 | 54.426 | . 882 | 100.00 | 13.953 | 59.486 | 1.055 |
| 150.00 | 12.052 | 58.990 | 1.448 | 150.00 | 17.010 | 65.729 | 1.831 |
| 200.00 | 13.549 | 62.654 | 2.087 | 200.00 | 19.808 | 71.000 | 2.752 |
| 250.00 | 15.295 | 65.856 | 2.807 | 250.00 | 22.658 | 75.716 | 3.813 |
| 298.00 | 17.182 | 68.696 | 3.586 | 298.00 | 25.509 | 79.930 | 4.969 |
| 300.00 | 17.264 | 68.811 | 3.620 | 300.00 | 25.629 | 80.101 | 5.020 |
| 400.00 | 21.368 | 74.331 | 5.553 | 400.00 | 31.553 | 88.277 | 7.882 |
| 500.00 | 25.110 | 79.501 | 7.881 | 500.00 | 36.860 | 95.890 | 11.309 |
| 600.00 | 28.292 | 84.360 | 10.556 | 600.00 | 41.348 | 103.007 | 15.226 |
| 700.00 | 30.981 | 88.922 | 13.523 | 700.00 | 45.126 | 109.663 | 19.555 |
| 800.00 | 33.282 | 93.207 | 16.739 | 800.00 | 48.345 | 115.896 | 24.232 |
| 900.00 | 35.272 | 97.240 | 20.169 | 900.00 | 51.119 | 121.747 | 29.209 |
| 1000.00 | 37.006 | 101.043 | 23.785 | 1000.00 | 53.527 | 127.254 | 34.444 |
| 1100.00 | 38.522 | 104.639 | 27.563 | 1100.00 | 55.626 | 132.451 | 39.904 |
| 1200.00 | 39.849 | 108.045 | 31.483 | 1200.00 | 57.458 | 137.367 | 45.560 |
| 1300.00 | 41.013 | 111.279 | 35.527 | 1300.00 | 59.059 | 142.026 | 51.388 |
| 1400.00 | 42.034 | 114.354 | 39.681 | 1400.00 | 60.461 | 146.452 | 57.366 |
| 1500.00 | 42.931 | 117.283 | 43.930 | 1500.00 | 61.691 | 150.663 | 63.474 |
| 2000.00 | 46.070 | 130.101 | 66.259 | 2000.00 | 65.971 | 169.048 | 95.499 |
| 2500.00 | 47.837 | 140.584 | 89.776 | 2500.00 | 68.368 | 184.044 | 129.137 |
| 3000.00 | 48.904 | 149.405 | 113.982 | 3000.00 | 69.809 | 196.643 | 163.710 |
| 3500.00 | 49.588 | 156.996 | 138.616 | 3500.00 | 70.731 | 207.476 | 198.861 |
| 4000.00 | 50.050 | 163.649 | 163.533 | 4000.00 | 71.354 | 216.962 | 234.391 |
| 4500.00 | 50.375 | 169.563 | 188.644 | 4500.00 | 71.792 | 225.392 | 270.184 |
| 5000.00 | 50.613 | 174.883 | 213.894 | 5000.00 | 72.110 | 232.973 | 306.163 |
| Zero Point Vibration Energy ( $\mathrm{kcal} / \mathrm{mol}$ ) $=48.9$ |  |  |  | Zero Point Vibration Energy (kcal/mol) $=67.5$ |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

Table B8 Ideal Gas-Phase Thermodynamic Property vs. Temperature ${ }^{\mathrm{a}}$ of $\mathrm{CH}_{3} \mathrm{SCH}_{2} \mathrm{OH}$, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCH}_{2} \mathrm{OH}, \mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ and $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$. (Continued)

| (c) $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ |  |  |  | (d) $\mathrm{CH}_{3} \mathrm{~S}(=\mathrm{O}) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  | T(K) | Cp | [ $\mathrm{H}(\mathrm{T})-\mathrm{H}(0 \mathrm{~K})$ ] |  |
|  | mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) |  | /mol/K) | ( $\mathrm{cal} / \mathrm{mol} / \mathrm{K}$ ) | ( $\mathrm{kcal} / \mathrm{mol}$ ) |
| 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 ( $\mathrm{kcal} / \mathrm{mol}$ ) $=69.3$ |  |  |  |

${ }^{\mathrm{a}}$ Thermodynamic properties are referred to standard state of an ideal gas at 1 atm .

## REFERENCES

1) Molecular Weight: http://www.webqc.org/mmcalc.php.
 (Accessed in 4/15/2011).
2) F. A. Carey, R. J. Sundberg, "Advance Organic Chemistry, Part A: Structure and Mechanisms, 4th ed.", Charlottesville, VA: Springer, 2004.
3) M. Munowitz, "Principles of Chemistry, $1^{\text {st }}$ ed.", QD133 M984, 2000.
4) 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.
5) Li Zhu and J. W. Bozzelli, The multi-channel reaction of $\mathrm{CH}_{3} \mathrm{~S}+\mathrm{O}_{2}$ : thermochemistry and kinetic barriers, J. Mol. Struct.: THERMOCHEM, vol: 728(2005) 147-157.
6) 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.
7) 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.
8) Frank Jensen, "Introduction to Computational Chemistry", New York: Wiley, c1999.
9) David C. Young, "Computational chemistry: a practical guide for applying techniques to real world problems", New York: Wiley, c1999.
10) 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) 10491058.
11) 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.
12) E. Frisch and Micheal J. Frisch, "Gaussian 03 Pocket Reference", Carnegie, PA: Gaussian Inc. March 2003.
13) NIST Webbook: http://webbook.nist.gov/chemistry/.
14) Daan Frenkel and Berend Smit: "Understanding Molecular Simulation From Alrorithms to Applications, $2^{\text {nd }}$ Edition", San Diego, CA: Elsevier, 2002.
15) S. Snitsiriwat and Joseph W. Bozzelli, The Thermochemistry and Bond Energies of Nitro-alkanes, -Alkenes, -Carbonyls and Corresponding Nitrites, NJIT Master Thesis, Jan. 2009.
16) F. Jin, J. Bozzelli, R. Asatryan, Thermodynamic and Kinetic Analysis on the Activation Reaction of Dimethyl Sulfide Radical with Oxygen, 2011, to be submitted.
17) Sh. P. Pillai, Structure and Thermochemistry of Disulfide-Oxygen Species, NJIT Master Thesis, Jan. 2008.
18) 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.
19) http://www.spaceref.com/news/viewpr.html?pid=10216 (Accessed in 05/02/2011).
20) Gary V. and Stephen D. "Environmental Chemistry, A Global Perspective, $2^{\text {nd }}$ Ed", Oxford, UK: Oxford University Press, 2005 P362.
21) http://en.wikipedia.org/wiki/Enthalpy_of_atomization (Accessed in 05/08/2011).
22) http://en.wikipedia.org/wiki/Standard_enthalpy_of_formation (Accessed in 05/08/2011).
23) Chad Sheng, Ph D Thesis, Chemical Engineering, New Jersey Institute of Technology, 2002.
