

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

STRUCTURE AND THERMOCHEMISTRY OF DISULFIDE-OXYGEN SPECIES

by
Shyamala Pravin Pillai

Sulfur compounds are known to form aerosols that can counteract the greenhouse effect, and recent studies suggest that aerosols can also contribute to global warming; sulfur species are also known as major contributors to acid rain. Both of these atmospheric chemistry interactions involve SO_2 , which is formed by oxidation of sulfur hydrocarbons and H_2S . This study describes the structure, internal rotor potentials, bond energies and determines thermochemical properties ($\Delta_f H^\circ$, S° and $C_p(T)$) on the S-S bridge system in the sulfur bridged molecules CH_3SSOH , $\text{CH}_3\text{SS}(=\text{O})\text{H}$, HSSOH , $\text{HSS}(=\text{O})\text{H}$ and $\text{CH}_3\text{SSOCH}_3$ and the their radicals corresponding to H atom loss. Structure and thermochemical parameters (S° and $C_p(T)$) are determined using Density Functional B3LYP/6-31G (d, p), B3LYP/6-311++G (3df, 2p) and composite CBS-QB3 ab initio computational chemistry calculations.

Enthalpies of formation for CH_3SSOH , $\text{CH}_3\text{SS}(=\text{O})\text{H}$, $\text{CH}_3\text{SS}^\bullet=\text{O}$ and $^\bullet\text{CH}_2\text{SSOH}$ are -38.46, -17.74, -17.02 and 7.17 kcal mol^{-1} respectively. The C—H Bond Energy of CH_3SSOH is 97.73 kcal mol^{-1} , and the O-H bond energy is weak at 73.54 kcal mol^{-1} . The weak O—H bond results because the CH_3SSOH parent undergoes electron re-arrangement upon loss of the $\text{CH}_3\text{SSO—H}$ hydrogen atom to form the more stable $\text{CH}_3\text{SS}^\bullet=\text{O}$ structure. The C—H bond energy of $\text{CH}_3\text{SS}(=\text{O})\text{H}$ is remarkably weak at only 77.01 kcal mol^{-1} and results in the formation of $^\bullet\text{CH}_2\text{SSOH}$ radical by the loss of H— $\text{CH}_2\text{SS}(=\text{O})\text{H}$ hydrogen atom, and the S-H bond energy is also weak. The very weak

S—H bond (only 52.82 kcal mol⁻¹) formed from loss of the CH₃SS(=O)—H hydrogen atom forms a CH₃SS[•]=O radical.

Enthalpies of formation for HSSOH, HSS(=O)H, HSS[•]=O and S[•]SOH are -33.62 (+/-0.2) kcal mol⁻¹, -12.88 (+/-0.2) kcal mol⁻¹, -14.44 (+/-0.2) kcal mol⁻¹ and -19.96 (+/-0.2) kcal mol⁻¹ respectively. The S—H Bond Energy of HSSOH is 65.76 kcal mol⁻¹, and the O-H bond energy is 71.28 kcal mol⁻¹. The S—H Bond Energy of H—SS(=O)H is weak at only 45.02 kcal mol⁻¹ and results in the formation of [•]SSOH radical by the loss of hydrogen atom, and the S-H bond energy of HSS(=O)—H is very weak at 50.54 kcal mol⁻¹. The very weak S—H bond, upon loss of the HSS(=O)—H hydrogen atom forms a more stable HSS[•]=O radical.

Enthalpies of formation for CH₃SSOCH₃ and the radical [•]CH₂SSOCH₃ are -34.33 kcal mol⁻¹ and 11.4 kcal mol⁻¹ respectively. It is important to note that as the CH₃SSOC[•]H₂ radical is formed it immediately dissociates to lower energy products CH₃SS[•](=O) + CH₂=O with no significant LT 6 kcal mol⁻¹) barriers. This CH₃SSOC[•]H₂ radical does not exist.

**STRUCTURE AND THERMOCHEMISTRY OF DISULFIDE-OXYGEN
SPECIES**

by
Shyamala Pravin Pillai

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

Department of Chemistry and Environmental Science

January 2008

Blank Page

APPROVAL PAGE

**STRUCTURE AND THERMOCHEMISTRY OF DISULFIDE-OXYGEN
SPECIES**

Shyamala Pravin Pillai

Dr. Joseph W. Bozzelli, Date
Distinguished Professor of Chemistry and Environmental Science, NJIT

Dr. Carol Venanzi, Date
Distinguished Professor of Chemistry and Environmental Science, NJIT

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

BIOGRAPHICAL SKETCH

Author: Shyamala Pravin Pillai
Degree: Master of Science in Chemistry
Date: January 2008

Undergraduate and Graduate Education:

- Master of Science in Chemistry,
New Jersey Institute of Technology, Newark, NJ, 2008
- Master of Science in Physical Chemistry,
University of Mumbai, Mumbai, India, 1995
- Bachelor of Science in Chemistry and Biochemistry,
University of Mumbai, Mumbai, India, 1993

Major: Chemistry

Publications:

Shyamala P. Pillai, J.W. Bozzelli, "Structural and Thermochemical Studies on S-S-O Bridged System in CH_3SSOH and Radicals Corresponding to Loss of H Atom", to be submitted to Journal of Molecular Structure: Thermochem, (2008).

Shyamala P. Pillai, J.W. Bozzelli, "Structural and Thermochemical Studies on S-S-O Bridged System in HSSOH and Radicals Corresponding to Loss of H Atom", to be submitted to Journal of Molecular Structure: Thermochem, (2008).

Shyamala P. Pillai, J.W. Bozzelli, "Structural and Thermochemical Studies on S-S Bridged System in $\text{CH}_3\text{SSOCH}_3$ and Radicals Corresponding to Loss of H Atom", to be submitted to Journal of Molecular Structure: Thermochem, (2008).

To my beloved son, Mayaank.

ACKNOWLEDGMENT

I take this opportunity to express my deepest appreciation to Dr. Joseph W. Bozzelli, who not only served as my research supervisor, providing valuable and countless resources, insight, but also constantly gave me support, encouragement, and reassurance. Special thanks are given to Dr. Li Zhu, Dr. Rubik Asatryan and Dr. Gabriel da Silva for sharing their knowledge resources with me. I would also like to thank Dr. Carol Venanzi and Dr. Tamara Gund for actively participating in my committee.

I also acknowledge partial funding for this research from Army Research Office Grant W911NF0410120.

TABLE OF CONTENTS

Chapter	Page
1 INTRODUCTION AND OBJECTIVE.....	1
2 STRUCTURAL AND THERMOCHEMICAL STUDIES ON S-S-O BRIDGED SYSTEM IN CH ₃ SSOH AND CH ₃ SS(=O)H AND THEIR RADICALS CORRESPONDING TO LOSS OF H ATOM.....	2
2.1 Introduction.....	2
2.2 Calculation Methods	4
2.3 Results and Discussion.....	5
2.3.1 Structure	5
2.3.2 Heats of Formation and Enthalpies of Reaction.....	10
2.3.3 Bond Energies.....	15
2.3.4 Frequencies and Moments of Inertia.....	17
2.3.5 Internal Rotational Potential.....	18
2.3.6 S ^o ₂₉₈ and Cp ^o (T).....	27
2.4 Summary.....	29
3 STRUCTURAL AND THERMOCHEMICAL STUDIES ON S-S-O BRIDGED SYSTEM IN HSSOH AND HSS(=O)H AND RADICALS CORRESPONDING TO LOSS OF H ATOM	30
3.1 Introduction.....	30
3.2 Calculation Methods	33
3.3 Results and Discussion.....	34
3.3.1 Structure	34
3.3.2 Heats of Formation and Enthalpies of Reaction.....	38

TABLE OF CONTENTS
(Continued)

Chapter	Page
3.3.3 Bond Energies.....	43
3.3.4 Frequencies and Moments of Inertia.....	44
3.3.5 Internal Rotational Potential.....	45
3.3.6 S°_{298} and $C_p^{\circ}(T)$	50
3.4 Summary.....	52
4 STRUCTURAL AND THERMOCHEMICAL STUDIES ON S-S-O BRIDGED SYSTEM IN CH_3SSOCH_3 AND RADICALS CORRESPONDING TO LOSS OF H ATOM.....	53
4.1 Introduction.....	53
4.2 Calculation Methods	55
4.3 Results and Discussion.....	56
4.3.1 Structure	56
4.3.2 Heats of Formation and Enthalpies of Reaction.....	60
4.3.3 Bond Energies.....	64
4.3.4 Frequencies and Moments of Inertia.....	64
4.3.5 Internal Rotational Potential.....	65
4.3.6 S°_{298} and $C_p^{\circ}(T)$	72
4.4 Summary.....	73
APPENDIX A ADDITIONAL DATA ON ENTROPY	74
APPENDIX B ADDITIONAL DATA ON HEAT CAPACITIES.....	78
APPENDIX C INPUT FILES FOR SMCPS.....	82
APPENDIX D INPUT FILES FOR INTERNAL ROTOR CONTRIBUTIONS CALCULATED BY ROTATOR PROGRAM.....	93

TABLE OF CONTENTS
(Continued)

Chapter	Page
APPENDIX E OPTIMIZED Z-MATRIX.....	105
APPENDIX F LIST OF ENERGIES.....	109
REFERENCES	112

LIST OF TABLES

Table		Page
2.1	Angles and Bond Distance From Optimized Geometry	6
2.2	Comparison of Lowest Energy Dihedral from PE curve with Structural Parameter	9
2.3	Mulliken Atomic Charges for the Molecules and their Radicals.....	10
2.4	Calculated $\Delta H_{\text{rxn}298}$ (kcal mol ⁻¹) from Isodesmic Reactions.....	12
2.5	Calculated Enthalpies of Formation (kcal mol ⁻¹) of Species in Isodesmic Work Reactions.....	13
2.6	Enthalpies of Formation of Reference Species in Work reaction.....	15
2.7	Bond Energy Calculation (kcal mol ⁻¹).....	16
2.8	Frequencies and Moments of Inertia.....	17
2.9	Entropy and Heat Capacities.....	28
3.1	Angles and Bond Distance from Optimized Geometry	35
3.2	Comparison of Lowest Energy Dihedral from PE curve with Structural Parameter	37
3.3	Mulliken Atomic Charges for the Molecules and their Radicals.....	38
3.4	Calculated $\Delta H_{\text{rxn}298}$ (kcal mol ⁻¹) from Isodesmic Reactions.....	40
3.5	Calculated Enthalpies of Formation (kcal mol ⁻¹) of Species in Isodesmic Work Reactions.....	41
3.6	Enthalpies of Formation of Reference Species in Work reaction.....	42
3.7	Bond Energy Calculation (kcal mol ⁻¹).....	43
3.8	Frequencies and Moments of Inertia.....	45
3.9	Entropy and Heat Capacities.....	51

LIST OF TABLES
(Continued)

Table	Page
4.1 Angles and Bond Distance from Optimized Geometry	57
4.2 Comparison of Lowest Energy Dihedral from PE curve with Structural Parameter	59
4.3 Mulliken Atomic Charges for the Molecules and their Radicals.....	59
4.4 Calculated $\Delta H_{\text{rxn}298}$ (kcal mol ⁻¹) from Isodesmic Reactions.....	61
4.5 Calculated Enthalpies of Formation (kcal mol ⁻¹) of Species in Isodesmic Work Reactions.....	62
4.6 Enthalpies of Formation of Reference Species in Work reaction.....	63
4.7 Bond Energy Calculation (kcal mol ⁻¹).....	64
4.8 Frequencies and Moments of Inertia.....	65
4.9 Entropy and Heat Capacities.....	72

LIST OF FIGURES

Figure		Page
2.1	Potential Energy Profile for the HC—S-(SOH) Rotor in CH ₃ SSOH Molecule.....	19
2.2	Potential Energy Profile for the (CH ₃)S—S(OH) Rotor in CH ₃ SSOH Molecule.....	19
2.3	Potential Energy Profile for the (CH ₃)SS—(OH) Rotor in CH ₃ SSOH Molecule.....	20
2.4	Potential Energy Profile for CH ₂ —S(SOH) Rotor in [*] CH ₂ SSOH Molecule.....	21
2.5	Potential Energy Profile for S—S rotor in [*] CH ₂ SSOH Molecule....	22
2.6	Potential energy profile for the CH ₂ S-S—O-H rotor in [*] CH ₂ SSOH Molecule.....	23
2.7	Potential Energy Profile for the H ₃ C—S(S [*] =O) Rotor in CH ₃ SS [*] =O...	24
2.8	Potential Energy Profile for the CH ₃ -S—S [*] =O Rotor in CH ₃ SS [*] =O Molecule.....	24
2.9	Potential Energy Profile for the H ₃ C—S-S(=O)H Rotor in CH ₃ SS(=O)H Molecule.....	25
2.10	Potential Energy Profile for the H ₃ C-S—S(=O)H Rotor in CH ₃ SS(=O)H Molecule.....	26
3.1	Potential Energy Profile for the HS—SOH Rotor in HSSOH Molecule...	46
3.2	Potential Energy Profile for the HSS—OH Rotor in HSSOH Molecule...	47
3.3	Potential Energy Profile for S-S—O-H Rotor in [*] SSOH Molecule.....	48
3.4	Potential Energy Profile for the HS— S [*] =O Rotor in H-SS [*] =O.....	49
3.5	Potential Energy Profile for the H-S—S(=O)H Rotor in HSS(=O)H Molecule	50

LIST OF FIGURES
(Continued)

Figure		Page
4.1	Potential Energy Profile for the H-C—S-(SOC) Rotor in CH ₃ SSOCH ₃ Molecule.....	66
4.2	Potential Energy Profile for the (CH ₃)S—S(OH) Rotor in CH ₃ SSOH Molecule.....	67
4.3	Potential Energy Profile for the (CH ₃ SS O—C) Rotor in CH ₃ SSOCH ₃ Molecule.....	67
4.4	Potential Energy Profile for CH ₃ S(S—OC) Rotor in CH ₃ SSOCH ₃ Molecule.....	68
4.5	Potential Energy Profile for C—S rotor in ·CH ₂ —SSOC Molecule...	69
4.6	Potential Energy Profile for the ·CH ₂ S—SOC Rotor in ·CH ₂ SSOCH ₃ Molecule	69
4.7	Potential Energy Profile for the ·CH ₂ S(S—OC) Rotor in ·CH ₂ SSOCH ₃ Molecule.....	70
4.8	Potential Energy Profile for the ·CH ₂ -SSO—C Rotor in ·CH ₂ SSOCH ₃ Molecule.....	71

LIST OF SYMBOLS

ΔH_{rxn}	Heat of Reaction
ΔH_f°	Heat of Formation
I	Moments of Inertia
S°_{298}	Entropy at 298 K
$C_p^\circ(T)$	Heat Capacity at Constant Temperature
PE Curve	Potential Energy Curve

CHAPTER 1

INTRODUCTION AND OBJECTIVES

This work describes the structure, internal rotor potentials and bond energies and determines thermochemical properties (ΔH_f° , S° and $C_p(T)$) on the S-S-O bridge systems. Structure and thermochemical parameters (S° and $C_p(T)$) are determined using Density Functional B3LYP/6-31G (d, p), B3LYP/6-311++G (3df, 2p) and composite CBS-QB3 ab initio computational chemistry calculations. Enthalpies of formation for stable species are calculated using the total energies at B3LYP/6-31G (d, p), B3LYP/6-311++G (3df, 2p), and CBS-QB3 levels with work reactions that areisodesmic in most cases. Contributions to S°_{298} and $C_p^\circ(T)$ of each species are calculated from the parameters determined using the B3LYP structures, frequencies, plus symmetry spin degeneracy and number of optical isomers. In place of the torsion frequency values the internal rotor potentials are analyzed and their contributions to entropy and heat capacity are included. Chapter 2 discuss about CH_3SSOH and $\text{CH}_3\text{SS}(=\text{O})\text{H}$ and the two radicals corresponding to H atom loss $\text{CH}_3\text{SS}^\bullet=\text{O}$ and $^\bullet\text{CH}_2\text{SSOH}$. Chapter 3 will deal with HSSOH and $\text{HSS}(=\text{O})\text{H}$ and the two radicals corresponding to H atom loss $\text{HSS}^\bullet=\text{O}$ and $^\bullet\text{SSOH}$. The two aforementioned radicals, $\text{CH}_3\text{SS}^\bullet=\text{O}$ and $^\bullet\text{CH}_2\text{SSOH}$, can originate from either or both the parent molecules viz: CH_3SSOH and $\text{CH}_3\text{SS}(=\text{O})\text{H}$. Similarly the radicals $\text{HSS}^\bullet=\text{O}$ and $^\bullet\text{SSOH}$ can originate from either or both the parent molecules viz: HSSOH and $\text{HSS}(=\text{O})\text{H}$. Chapter 4 talks on the $\text{CH}_3\text{SSOCH}_3$ and its radicals $^\bullet\text{CH}_2\text{SSOCH}_3$ and $\text{CH}_3\text{SSOC}^\bullet\text{H}_2$.

CHAPTER 2

STRUCTURAL AND THERMOCHEMICAL STUDIES ON S-S-O BRIDGED SYSTEM IN CH_3SSOH AND $\text{CH}_3\text{SS}(=\text{O})\text{H}$ AND THEIR RADICALS CORRESPONDING TO LOSS OF H ATOM

2.1 Introduction

Atmospheric sulfur chemistry is important in climate change because both naturally and anthropogenically emitted sulfur compounds form minute particles in the atmosphere (aerosols) that reflect solar and absorb IR radiation; they also affect production of atmospheric haze, acid rain, and ozone depletion. These sulfur oxide particles may also act as condensation nuclei for water vapor and enhance global cloudiness. The primary natural sources of sulfur are volcanic emissions and dimethylsulfide production by oceanic phytoplankton [1].

Human impact on the sulfur cycle is primarily in the production of sulfur dioxide (SO_2) from industry (e.g. burning coal) and the internal combustion engine. Sulfur dioxide can precipitate onto surfaces where it can be oxidized to sulfate in the soil (it is also toxic to some plants), reduced to sulfide in the atmosphere, or oxidized to sulfate in the atmosphere as sulfuric acid, a principal component of acid rain [2].

Studies are underway to carry out details on the reactivity and stability of the sulfur compounds and their radicals and also to know the kinetics and thermochemistry involved in their reaction process. The reaction of methylthiyl radical ($\text{CH}_3\text{S}\cdot$) with $^3\text{O}_2$ is a potentially important process for both combustion and atmospheric chemistry as a pathway for the exothermic conversion (oxidation) of CH_3S . This reaction system also serves as a surrogate reaction system for a number of paths in longer chain and

substituted thiol radical reactions with molecular oxygen [3]. This $\text{CH}_3\text{S} + \text{O}_2 \leftrightarrow \text{CH}_3\text{S}-\text{OO}$ reaction has a very shallow well, $\sim 10 \text{ kcal mol}^{-1}$, which results in very rapid reverse reaction to back to $\text{CH}_3\text{S}\cdot$ and a quasi equilibrium. The CH_3S and CH_3SOO can react with hydroperoxides (e.g. HO_2 , $\text{CH}_3\text{SOO}\cdot$) or OH or NO_x to form the CH_3SO moiety, which exists as $\text{CH}_3\text{S}\cdot(=\text{O})$.

With the rapid rise of economic development, acid rain has become one of the ten most serious problems which threaten the world environment [4]. $\text{CH}_3\text{S}\cdot(=\text{O})$ has been postulated as one of the key intermediates in the DMS oxidation mechanism. It may play an important role in the formation of acid rain because the bond length of the C—S bond is longer than that in CH_3S . The principal mechanism of SO_2 formation has been suggested to include a sequence of reactions of the $\text{CH}_3\text{S}\cdot(=\text{O})$ radical with O_2 , NO_2 , and O_3 as well as the thermal decomposition of CH_3-SO_2 [5].

It has been shown that the $\text{CH}_3\text{SS}\cdot(=\text{O})$ radical can be formed by the reaction $\text{CH}_3\text{SS} + \text{NO}_2 \rightarrow \text{CH}_3\text{SS}\cdot(=\text{O}) + \text{NO}$ and $\text{CH}_3\text{SS}\cdot(=\text{O})$ can potentially react with NO_2 to give several products [15]. Until now, however, there has been no theoretical or experimental study on the stability and thermochemical properties of CH_3SSOH and its radicals. Thus, a detailed knowledge about structure, bond energies, internal rotor potentials and the thermochemical properties of the disulfur methyl thiols and its reactions to radicals from loss of H is desirable to help in understanding its effect on environment.

2.2 Calculation Method

The structure and thermochemical parameters of CH₃SSOH are based on the density functional and composite ab initio levels using Gaussian 03 [6]. Computation levels include B3LYP/6-31G(d,p), B3LYP/6-311++G(3df,2p). The CBS-QB3 methods are utilized for improved energies and analysis.

The enthalpies of formation for stable species are calculated using the total energies at B3LYP/6-31G(d,p), B3LYP/6-311++G(3df,2p), and CBS-QB3 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 [7] 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. Contributions to S°_{298} and $C_p^{\circ}(T)$ of each species are calculated using the “SMCPS” (Statistical Mechanics for Heat Capacity and Entropy C_p and S) program[8] which incorporates the frequencies, moments of inertia, mass, symmetry, number of optical isomers, from the Gaussian calculation. It also incorporates frequency corrections. Torsion frequencies are omitted in SMCPS [8] calculation, and the “ROTATOR” program [8-10] is used for contributions from internal rotations that are less than 3.0 kcal to S°_{298} and $C_p^{\circ}(T)$.

2.3 Results and Discussion

2.3.1 Structure

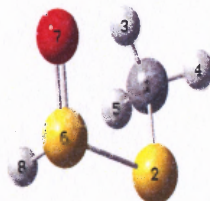
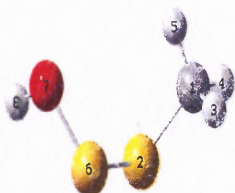
The S—O bond in CH₃SSOH is 1.69 Å, while S—O bond distance in CH₃SS=O exhibits shorter bond length of 1.51 Å. The C—S bond in CH₃SSOH is 1.83 Å against the 1.72 Å in •CH₂SSOH. In CH₃SS(=O)H, the S—O bond is 1.5 Å and the C—S bond is 1.83 Å. The shorter bond distance of 1.51 Å in S-O bond in CH₃SS=O predicts the presence of double bond.

The formation of CH₃SS=O is accompanied by reduction of the S-S-C bond angle to 99.13°, while formation of •C-H₂SSOH reveals increase in bond angle S-S-C to 105.6° compared to the S-S-C bond angle of 103.87° in CH₃SSOH as listed in Table 2.1.

Table 2.1 Angles and bond distances from optimized Geometry using B3LYP/6-31G(d,p)

CH₃SSOH

CH₃SS(=O)H

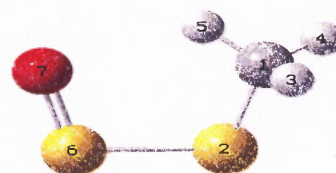


R1	R(1,2)	1.838
R2	R(1,3)	1.090
R3	R(1,4)	1.093
R4	R(1,5)	1.090
R5	R(2,6)	2.055
R6	R(6,7)	1.696
R7	R(7,8)	0.970
A1	A(2,1,3)	110.55
A2	A(2,1,4)	106.32
A3	A(2,1,5)	110.10
A4	A(3,1,4)	109.68
A5	A(3,1,5)	110.52
A6	A(4,1,5)	109.53
A7	A(1,2,6)	103.87
A8	A(2,6,7)	106.420

R1	R(1,2)	1.830
R2	R(1,3)	1.094
R3	R(1,4)	1.091
R4	R(1,5)	1.091
R5	R(2,6)	2.183
R6	R(6,7)	1.503
R7	R(6,8)	1.387
A1	A(2,1,3)	108.10
A2	A(2,1,4)	107.29
A3	A(2,1,5)	111.44
A4	A(3,1,4)	109.04
A5	A(3,1,5)	110.71
A6	A(4,1,5)	110.12
A7	A(1,2,6)	97.26
A8	A(2,6,7)	110.12

Table 2.1 Continued

A9	A(6,7,8)	106.611	A9	A(2,6,8)	91.98
D1	D(3,1,2,6)	59.383	A10	A(7,6,8)	106.52
D2	D(4,1,2,6)	178.383	D1	D(3,1,2,6)	33.34
D3	D(5,1,2,6)	-63.038	D2	D(4,1,2,6)	150.82
D4	D(1,2,6,7)	81.933	D3	D(5,1,2,6)	-88.5496
D5	D(2,6,7,8)	84.948	D4	D(1,2,6,7)	-39.1412
			D5	D(1,2,6,8)	69.275

 **$\cdot\text{CH}_2\text{SSOH}$**

R1	R(1,2)	1.727
R2	R(1,3)	1.082
R3	R(1,4)	1.083
R4	R(2,5)	2.087
R5	R(5,6)	1.693
R6	R(6,7)	0.970
A1	A(2,1,3)	120.93
A2	A(2,1,4)	117.55
A3	A(3,1,4)	121.49

 $\text{CH}_3\text{SS}^*(=\text{O})$

R1	R(1,2)	1.830
R2	R(1,3)	1.090
R3	R(1,4)	1.090
R4	R(1,5)	1.093
R5	R(2,6)	2.153
R6	R(6,7)	1.516
A1	A(2,1,3)	110.67
A2	A(2,1,4)	107.04
A3	A(2,1,5)	108.66

Table 2.1 Continued

A4	A(1,2,5)	105.60	A4	A(3,1,4)	110.37
A5	A(2,5,6)	106.97	A5	A(3,1,5)	110.44
A6	A(5,6,7)	106.71	A6	A(4,1,5)	109.54
D1	D(3,1,2,5)	29.728	A7	A(1,2,6)	99.13
D2	D(4,1,2,5)	-149.51	A8	A(2,6,7)	109.23
D3	D(1,2,5,6)	80.454	D1	D(3,1,2,6)	91.794
D4	D(2,5,6,7)	85.405	D2	D(4,1,2,6)	-147.870
			D3	D(5,1,2,6)	-29.648
			D4	D(1,2,6,7)	24.4624

The lowest energy structure for the individual species has been confirmed by comparing the lowest energy dihedral from the internal rotational potential curve with the structural parameter obtained from B3LYP/6-31G(d,p) of the parent molecule as shown in Table 2.2. Table 2.3 refers to the Mulliken atomic charges for the molecules and their radicals.

Table 2.2 Comparison of Lowest Energy Dihedral from PE Curve with Structural Parameter (see Figures 2.1 to 2.10)

Species	Potential curve	Structural Parameter	Dihedral
CH ₃ SSOH	Figure 1	D(3,1,2,6)	59.383
	Figure 2	D(1,2,6,7)	81.9337
	Figure 3	D(2,6,7,8)	84.9489
·CH ₂ SSOH	Figure 4	D(3,1,2,5)	29.7289
	Figure 5	D(1,2,5,6)	80.4543
	Figure 6	D(2,5,6,7)	85.4059
CH ₃ SS·=O	Figure 7	D(3,1,2,6)	91.7948
	Figure 8	D(1,2,6,7)	24.4624
CH ₃ SS(=O)H	Figure 9	D(4,1,2,6)	150.82
	Figure 10	D(1,2,6,8)	69.27

Table 2.3 reveals, the C—S, S—O bonds in CH₃SSOH and CH₃SS(=O)H and S=O bond in CH₃SS·=O are all polar covalent bonds. In CH₃SSOH, the S—O bond is more polar than the C—S bond due to higher degree of electro negativity / electron density on S atom of S—O bond. Hence it is obvious that the bond distance of S—O (1.69 Å) is shorter than C—S (1.84 Å) bond in CH₃SSOH. The C—S bond in ·CH₂SSOH is 1.72Å and is slightly shorter than the C—S bond in CH₃SSOH. This is due to the fact that the C atom possesses an extra electron which imparts partial negative charge to the C of C—S bond in CH₃SSOH.

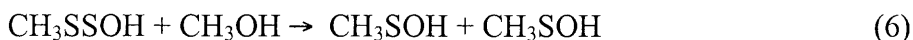
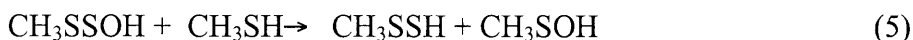
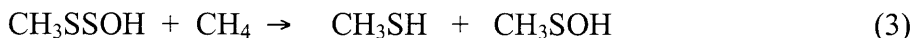
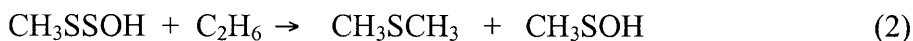
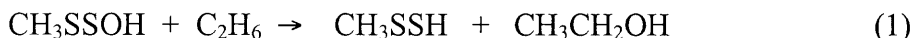
Table 2.3 Mulliken atomic charges for the molecules and their derived radicals

CH ₃ SSOH		CH ₃ SS(=O)H		CH ₃ SS·=O		·CH ₂ SSOH	
Atoms	Charges	Atoms	Charges	Atoms	Charges	Atoms	Charges
1 C	-0.465	1 C	-0.492	1 C	-0.487	1 C	-0.383
2 S	0.014	2 S	-0.040	2 S	-0.021	2 S	0.079
3 H	0.157	3 H	0.185	3 H	0.159	3 H	0.158
4 H	0.148	4 H	0.163	4 H	0.162	4 H	0.151
5 H	0.162	5 H	0.148	5 H	0.188	5 S	0.213
6 S	0.213	6 S	0.578	6 S	0.471	6 O	-0.556
7 O	-0.566	7 O	-0.562	7 O	-0.473	7 H	0.337
8 H	0.335	8 H	0.019				

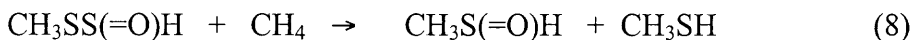
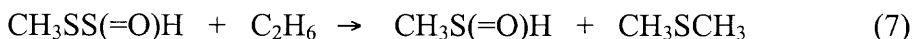
2.3.2 Heats of Formation and Enthalpies of Reaction

The following work reactions are used to calculate the heat of reaction and enthalpies of formation for CH₃SSOH and CH₃SS(=O)H molecule and their two radicals, CH₃SS·=O and ·CH₂SSOH respectively. The enthalpy calculations are based on the lowest energy conformer.

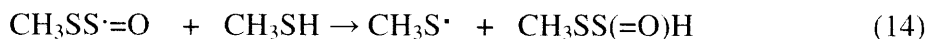
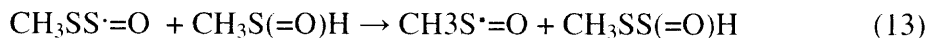
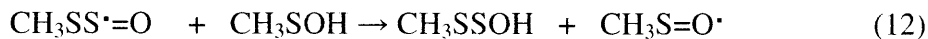
Work reactions for CH₃SSOH:



Work reactions for CH₃SS(=O)H:



Work reactions for $\text{CH}_3\text{SS}^{\cdot}=\text{O}$:



Work reactions for $\cdot\text{CH}_2\text{SSOH}$



Table 2.4 illustrates the comparative study on enthalpies of reaction for the above reactions. Table 2.5 compares the heat of formation for the Species under study using various levels of calculations. Similar calculations were also run for the reference species whose literature values are listed in table 2.6.

Table 2.4 Calculated $\Delta H_{\text{rxn}(298)}$ (kcal mol⁻¹) from isodesmic reactions.

Isodesmic reaction	B3LYP/6-31G (d, p)	B3LYP/6-311++G (3df, 2p)	CBSQB3
<i>Work reactions for CH₃SSOH:</i>			
CH ₃ SSOH + C ₂ H ₆ → CH ₃ SSH + CH ₃ CH ₂ OH	-1.75	0.1417	-8.59
CH ₃ SSOH + C ₂ H ₆ → CH ₃ SCH ₃ + CH ₃ SOH	13.28	15.08	12.12
CH ₃ SSOH + CH ₄ → CH ₃ SH + CH ₃ SOH	14.15	15.61	11.68
CH ₃ 3SSOH + HSH → CH ₃ SOH + HSSH	16.99	16.97	17.49
CH ₃ SSOH + CH ₃ SH → CH ₃ SSH + CH ₃ SOH	13.55	13.67	7.837
CH ₃ SSOH + CH ₃ OH → CH ₃ SOH + CH ₃ SOH	20.98	20.78	20.81
<i>Work reactions for CH₃SS(=O)H:</i>			
CH ₃ SS(=O)H + C ₂ H ₆ → CH ₃ S(=O)H + CH ₃ SCH ₃	6.61	7.31	6.93
CH ₃ SS(=O)H + CH ₄ → CH ₃ S(=O)H + CH ₃ SH	7.49	7.85	8.45
CH ₃ SS(=O)H + CH ₃ OH → CH ₃ S(=O)H + CH ₃ SOH	14.31	13.02	13.67
<i>Work reactions for CH₃SS=O:</i>			
CH ₃ SS=O + CH ₃ OH → CH ₃ SSOH + CH ₃ O·	24.66	29.46	33.78
CH ₃ SS=O + C ₂ H ₅ OH → CH ₃ SSOH + C ₂ H ₅ O·	26.79	31.73	33.25
CH ₃ SS=O + CH ₃ 3S(=O)H → CH ₃ S=O + CH ₃ SS(=O)H	0.3612	-11.18	-1.078
CH ₃ SS=O + CH ₃ SH → CH ₃ S· + CH ₃ SS(=O)H	-33.79	-30.28	-31.08
CH ₃ SS=O + CH ₃ SOH → CH ₃ SSOH + CH ₃ S=O	-6.30	-6.64	-6.06
<i>Work reactions for ·CH₂SSOH :</i>			
·CH ₂ SSOH + CH ₃ SH → CH ₃ SSOH + ·CH ₂ SH	-0.8383	-1.20	-2.21
·CH ₂ SSOH + C ₂ H ₅ S → CH ₃ SSOH + CH ₃ ·CHSH	-3.73	-3.44	-3.703
·CH ₂ SSOH + CH ₃ SCH ₃ → CH ₃ SSOH + ·CH ₂ SCH ₃	-2.04	-2.72	-3.459

Table 2.5 Calculated Enthalpies of formation (kcal mol⁻¹) of species in isodesmic work reaction

Isodesmic reaction	B3LYP/6-31G(d,p)	B3LYP/6-311++G(3df,2p)	CBSQB3
<i>Enthalpies of Formation of CH₃SSOH:</i>			
CH ₃ SSOH + C ₂ H ₆ → CH ₃ SSH + CH ₃ CH ₂ OH	-35.62	-37.46	-34.17
CH ₃ SSOH + C ₂ H ₆ → CH ₃ SCH ₃ + CH ₃ SOH	-36.08	-37.88	-36.88
CH ₃ SSOH + CH ₄ → CH ₃ SH + CH ₃ SOH	-35.63	-37.09	-37.08
CH ₃ SSOH + HSH → CH ₃ SOH + HSSH	-42.02	-41.99	-42.51
CH ₃ SSOH + CH ₃ SH → CH ₃ SSH + CH ₃ SOH	-43.22	-43.35	-37.51
CH ₃ SSOH + CH ₃ OH → CH ₃ SOH + CH ₃ SOH	-41.74	-42.55	-42.58
Average	-39.05	-40.05	- 38.46
<i>Mean of averages</i>	-39.19		
<i>Enthalpies of Formation of CH₃SS(=O)H:</i>			
CH ₃ SS(=O)H + C ₂ H ₆ → CH ₃ S(=O)H + CH ₃ SCH	-16.11	-16.81	-16.43
CH ₃ SS(=O)H + CH ₄ → CH ₃ S(=O)H + CH ₃ SH	-15.67	-16.03	-16.64
CH ₃ SS(=O)H + CH ₃ OH → CH ₃ S(=O)H + CH ₃ SOH	-20.77	-19.48	-20.14
Average	-17.52	-17.44	-17.74
<i>Mean of averages</i>	-17.57		

Table 2.5 continued

Isodesmic reaction	B3LYP/6-31G(d,p)	B3LYP/6-311++G(3df,2p)	CBSQB3
<i>Enthalpies of Formation of CH₃SS'=O:</i>			
CH ₃ SS'=O + CH ₃ OH → CH ₃ SSOH + CH ₃ O [•]	-11.97	-15.78	-20.10
CH ₃ SS'=O + C ₂ H ₅ OH → CH ₃ SSOH + C ₂ H ₅ O [•]	-12.97	-17.92	-19.45
CH ₃ SS'=O + CH ₃ S(=O)H → CH ₃ S'=O + CH ₃ SS(=O)H	-15.81	-16.57	-16.53
CH ₃ SS'=O + CH ₃ SH → CH ₃ S' + CH ₃ SS(=O)H	-16.16	-12.66	-13.45
CH ₃ SS'=O + CH ₃ SOH → CH ₃ SSOH + CH ₃ S'=O	-16.56	-16.22	-15.80
Average	-14.92	-15.83	-17.02
<i>Mean of averages</i>	-15.92		
<i>Enthalpies of Formation of [•]CH₂SSOH</i>			
[•] CH ₂ SSOH + CH ₃ SH → CH ₃ SSOH + [•] CH ₂ SH	5.55	5.92	6.92
[•] CH ₂ SSOH + C ₂ H ₅ SH → CH ₃ SSOH + CH ₃ [•] CHSH	6.89	6.61	6.87
[•] CH ₂ SSOH + CH ₃ SCH ₃ → CH ₃ SSOH + [•] CH ₂ SCH ₃	6.30	6.98	7.72
Average	6.25	6.50	7.17
<i>Mean of averages</i>	6.64		

Table 2.6 Enthalpies of formation (in kcal mol⁻¹) of reference species in work reactions

Species	ΔH_{f298}°	Species	ΔH_{f298}°
H [11]	52.1	C ₂ H ₆ [17]	-20.04
CH ₄ [16]	-17.89	CH ₃ SSH [20]	-1.24
CH ₃ SCH ₃ [11]	-8.94	CH ₃ SH [20]	-5.47
C ₂ H ₅ OH [19]	-56.17	CH ₃ SOH [14]	-33.9
C ₂ H ₅ SH [12]	-10.99	CH ₃ OH [19]	-48.04
·CH ₂ SCH ₃ [12]	33.78	CH ₃ ·CHSH [28]	30.64
·CH ₂ SH [3]	37.7	CH ₃ SO· [13]	18.31
C ₂ H ₅ O· [28]	-3.9	CH ₃ O· [18]	4.1
CH ₃ S(=O)H [21]	-20.6		

Of the above three methods, used in the calculation of enthalpies of formation of several species, B3LYP/6-31G(d,p) did not give satisfactory results due to smaller basis set. The results of B3LYP/6-311++G(3df,2p) are closer to CBS-QB3 composite method. Since we obtain very good agreement with the CBS-QB3 method for all of the work reactions and as the composite CBS-QB3 method has an advantage of utilizing geometry and frequencies calculated at the same level of theory, the CBS-QB3 composite method is recommended for thermo chemical determination on these S-S-O bridge systems.

2.3.3 Bond Energies

The bond energy of C—H bond in CH₃SSOH is calculated using [CH₃SSOH- [(H· + ·CH₂SSOH)]] reaction and the bond energy of O—H in CH₃SSOH is calculated using [CH₃SSOH- [(H· + CH₃SSO·)]]. Similarly, the bond energy of C—H bond in

$\text{CH}_3\text{SS}(=\text{O})\text{H}$ is calculated using $[\text{CH}_3\text{SS}(=\text{O})\text{H} - [(\text{H}\cdot + \cdot\text{CH}_2\text{SSOH})]]$ reaction and the bond energy of S—H in CH_3SSOH is calculated using $[\text{CH}_3\text{SS}(=\text{O})\text{H} - [(\text{H}\cdot + \text{CH}_3\text{SS}\cdot=\text{O})]]$ as shown in Table 2.7.

Table 2.7 Bond energy calculation in kcal/mole.

Bond Energy for	B3LYP/6-311G(d,p)	B3LYP/6-311G(3df,2p)	CBSQB3	Average
<i>CH_3SSOH:</i>				
C-H bond	-97.4	-98.65	-97.73	-97.93
O-H bond	-76.23	-76.32	-73.54	-75.36
<i>$\text{CH}_3\text{SS}(=\text{O})\text{H}$:</i>				
C-H bond	-75.87	-76.04	-77.01	-76.31
S-H bond	-54.70	-53.71	-52.82	-53.74

**average Hf values from Table 2.5 have been used to calculate the bond energy*

Thus the bond energy of C—H bond in CH_3SSOH is 97.73 kcal mol⁻¹. And the bond energy of O—H in CH_3SSOH is 75.54 kcal mol⁻¹. Thus the O—H bond is stronger than C—H bond in CH_3SSOH . Similarly, the C—H bond in $\text{CH}_3\text{SS}(=\text{O})\text{H}$ is 77.01 kcal mol⁻¹. And the bond energy of S—H in $\text{CH}_3\text{SS}(=\text{O})\text{H}$ is 52.82 kcal mol⁻¹.

2.3.4 Frequencies and Moment of Inertia

The frequencies and the moment of inertia help to identify the species using spectroscopic methods like FTIR. The list of the frequencies and the moments of inertia of the parent molecules and the corresponding radicals are listed in Table 2.8.

Table 2.8 Frequencies and moments of inertia

Species	Moment of Inertia, units $\text{amu}(\text{Bohr})^2$			frequencies (cm ⁻¹)					
	<i>I</i> 1	<i>I</i> 2	<i>I</i> 3	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
CH ₃ SSOH	203.44971	664.79585	728.21371	112.6	(139.5)**	230.4	279.3	448.4	496.2
				680.7	721.9	978.1	983.7	1189.1	1361.1
				1475.1	1491.7	3065.2	3159.2	3177	3763.8
CH ₃ SS(=O)H	217.27895	569.62069	725.95448	99.7	(184.9)	204.9	326.4	405.8	697.1
				831.0	990.2	996.9	1076.0	1100.6	1368.3
				1484.7	1498.8	2350.2	3050.7	3144.4	3166.7
•CH ₂ SSOH	185.80059	654.61197	711.35111	116.2	(201.3)	221.1	277.2	400.9	460.2
				467.7	722.7	787.1	934.0	1189.6	1409.7
				3169.5	3303.2	3760.6			
CH ₃ SS'=O	211.85814	533.28842	720.50403	(51.3)	(115.4)	221.1	353.0	436.4	694.4
				982.2	995.3	1069.7	1365.9	1482.2	493.7
				3062.9	3159.1	3174.3			

**Frequencies in bold corresponds to torsions that are removed in the SMCPs Analysis*

2.3.5 Internal Rotational Potential

The parent CH_3SSOH and corresponding methyl radical $\cdot\text{CH}_2\text{SSOH}$ has three internal rotors, while $\text{CH}_3\text{SS}^=\text{O}$ and $\text{CH}_3\text{SS}(=\text{O})\text{H}$ have only two. In these disulfide molecules we find the methyl rotors are somewhat similar to those in hydrocarbons with barriers near and below 3 kcal mol^{-1} , and the CS—SO and CSS-OR rotors have barriers near 5 kcal mol^{-1} or higher. In our entropy analysis, rotors with energy barriers greater than 3.0 kcal are not included in entropy and heat capacity calculations. Rotations about the $\text{H}_3\text{C—SS}$ bond in CH_3SSOH , the $\text{H}_3\text{C—SS}$ and CS—SO bonds in $\text{CH}_3\text{SS}^=\text{O}$, $\text{H}_3\text{C—SS}$ bond in $\text{CH}_3\text{SS}(=\text{O})\text{H}$ and the $\text{H}_2\text{C—SS}$ bond in $\cdot\text{CH}_2\text{SSOH}$ have energy barriers less than 3.0 kcal . Contributions to these internal rotors are calculated with Rotator program [8-10], and used instead of the contribution from the torsion frequency estimation in the Gaussian calculation.

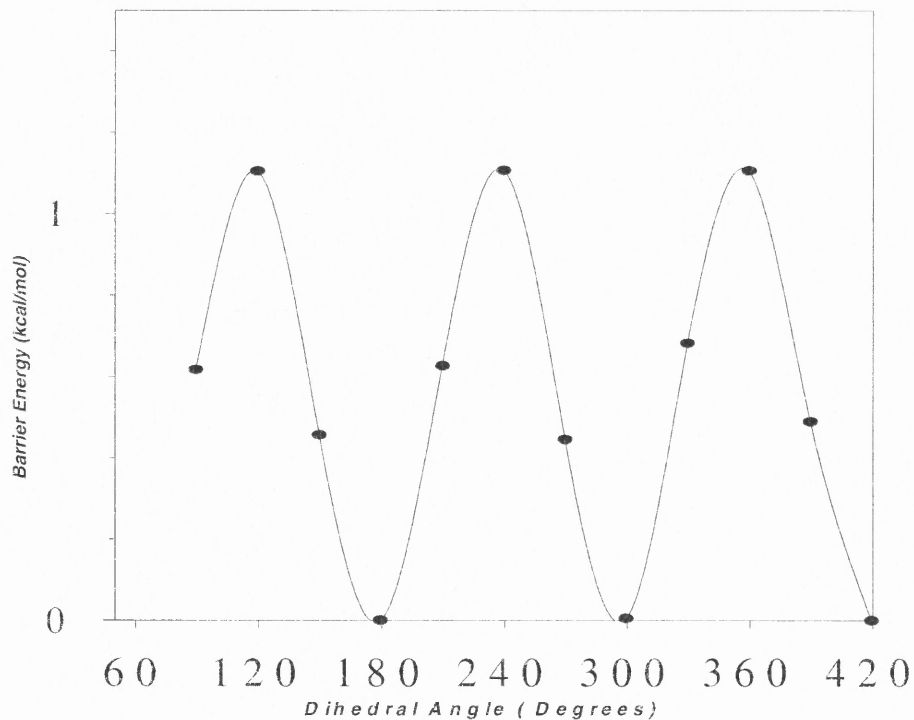


Figure 2.1 Potential energy profile for the H-C—S-(SOH) rotor in CH₃SSOH molecule

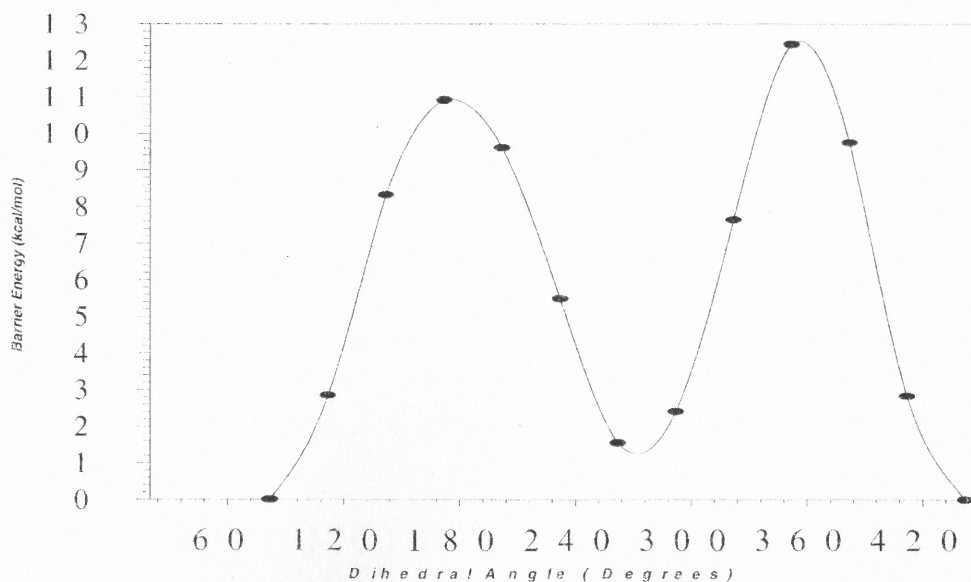


Figure 2.2 Potential energy profile for the (CH₃)S—S(OH) rotor in CH₃SSOH molecule

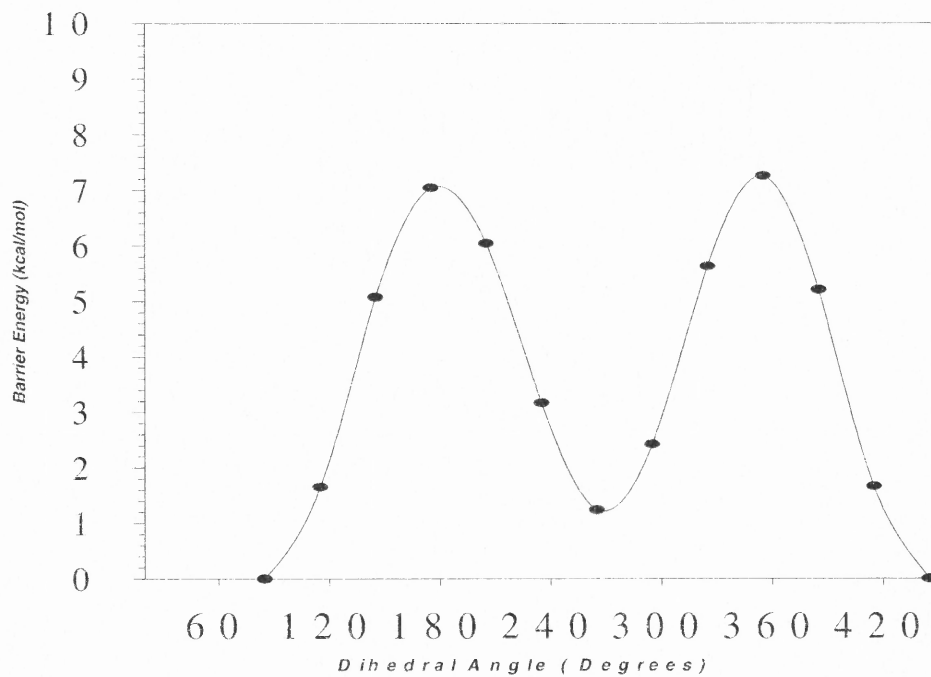


Figure 2.3 Potential energy profile for the (CH₃)SS—(OH) rotor in CH₃SSOH molecule

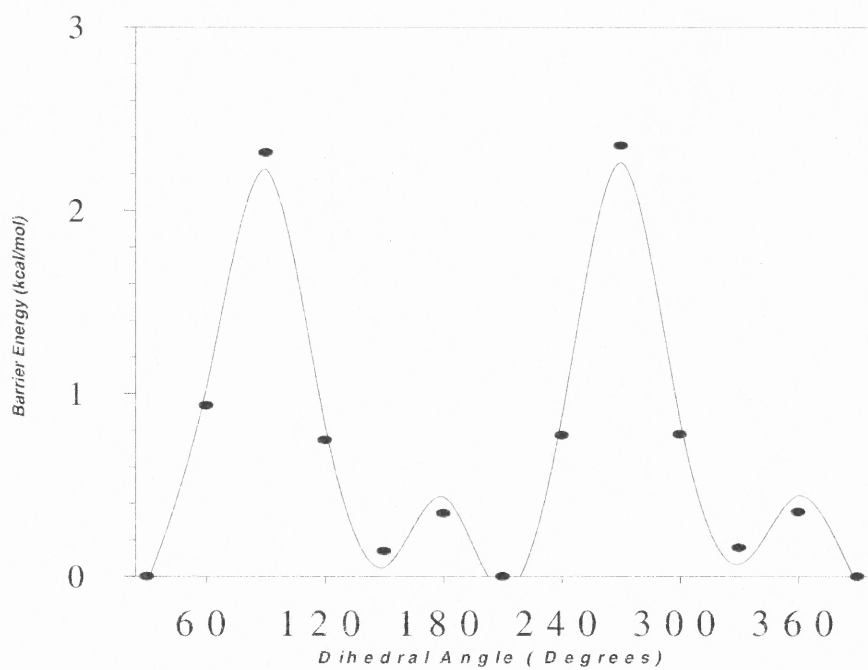


Figure 2.4 Potential energy profile for CH₂-S(SOH) rotor in CH₂SSOH molecule

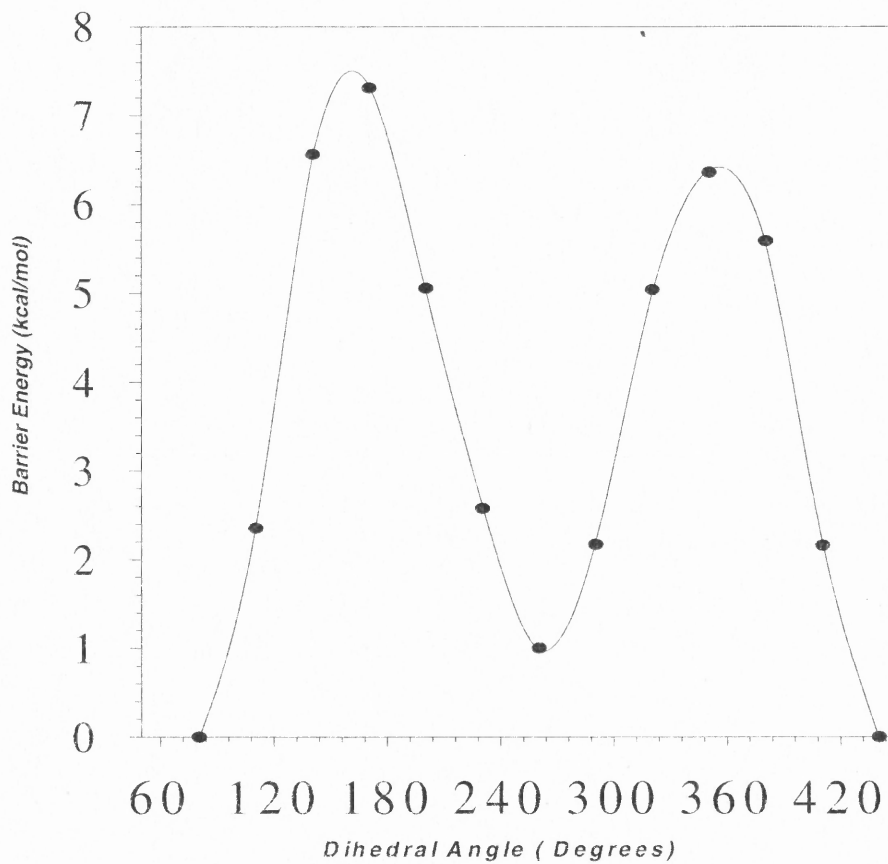


Figure 2.5 Potential energy profile for S—S rotor in $\text{CH}_2\text{S--SOH}$ molecule

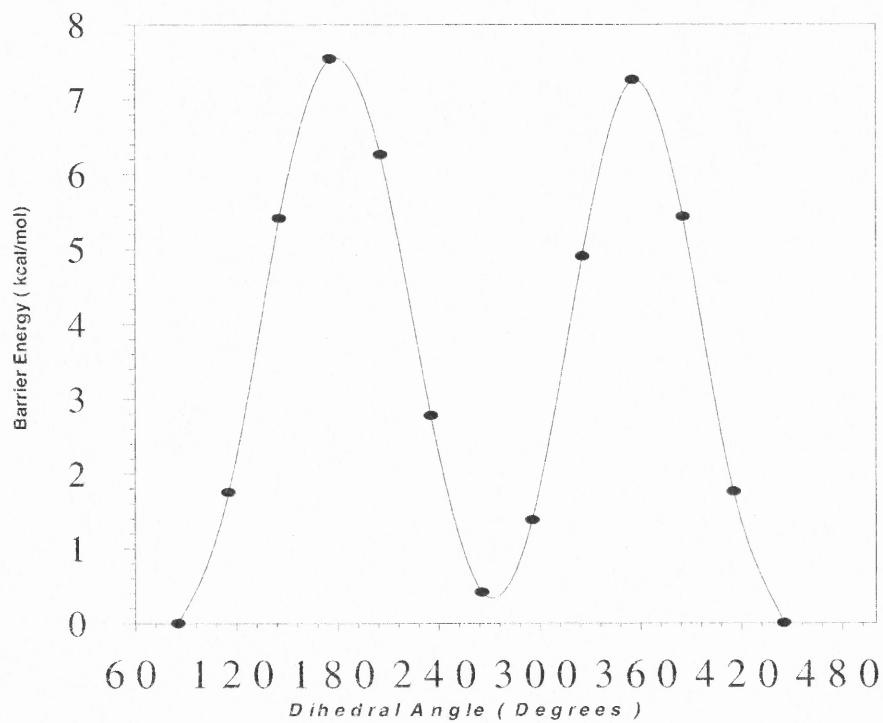


Figure 2.6 Potential energy profile for the CH₂S-S—O-H rotor in CH₂SSOH molecule

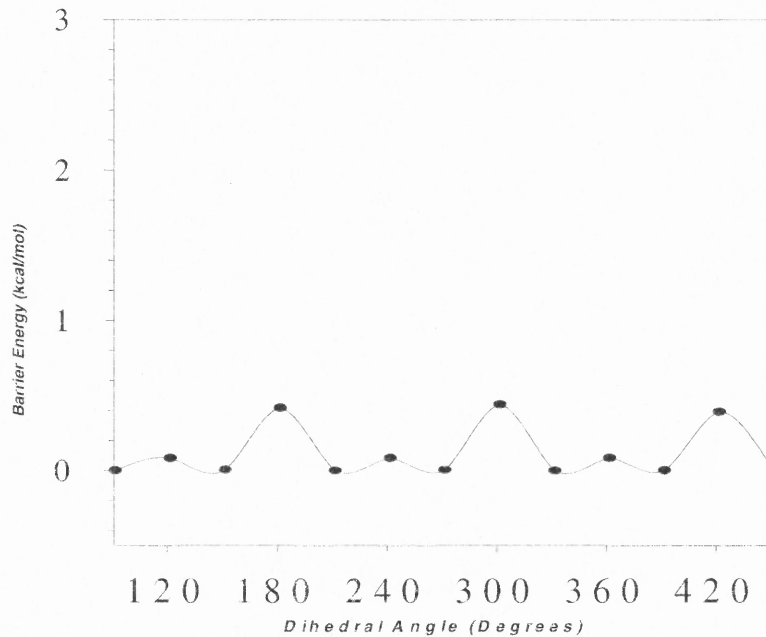
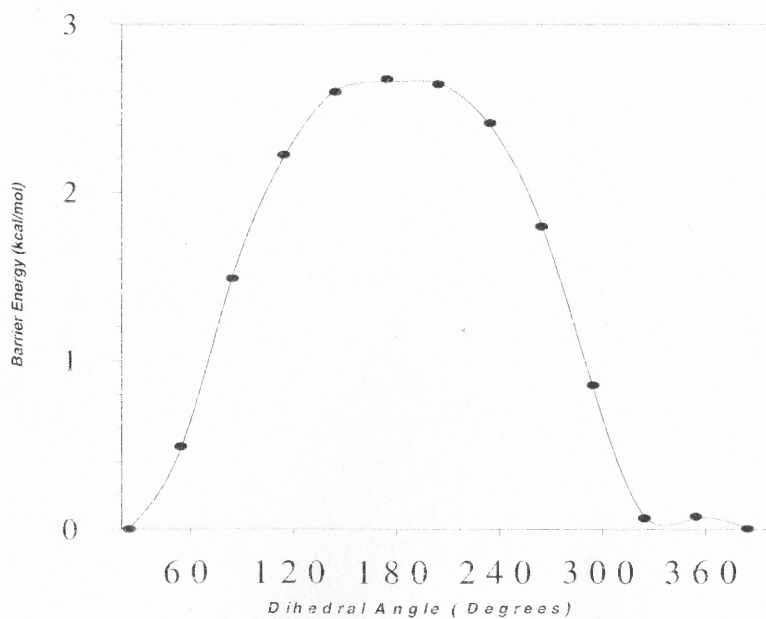


Figure 2.7 Potential energy profile for the H₃C—S(S'=O) rotor in CH₃--SS'=O.



2.8 Potential energy profile for the CH₃-S—S'=O rotor in CH₃SS'=O molecule

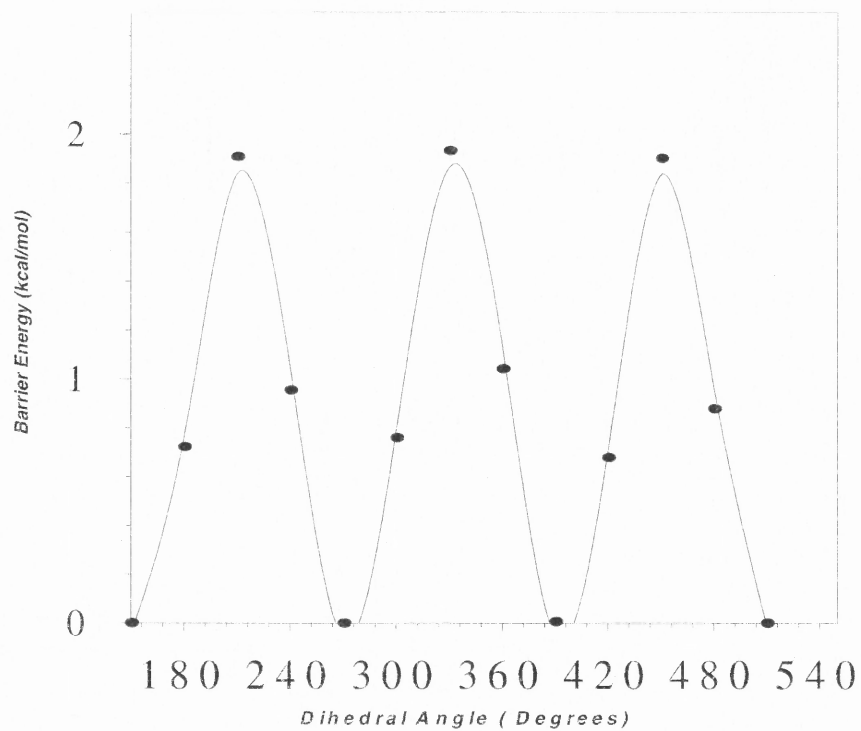


Figure 2.9 Potential energy profile for the $\text{H}_3\text{C}-\text{S}-\text{S}(=\text{O})\text{H}$ rotor in $\text{CH}_3\text{SS}(=\text{O})\text{H}$ molecule

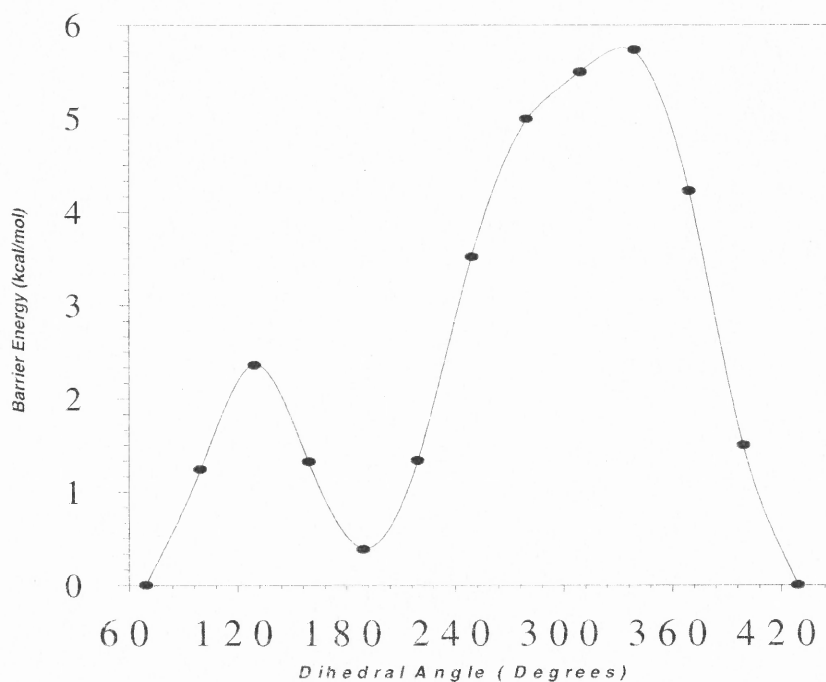


Figure 2.10 Potential energy profile for the $\text{H}_3\text{C-S-S(=O)H}$ rotor in $\text{CH}_3\text{SS(=O)H}$ molecule

The C—S rotors studied so far have the barrier near and below 3 kcal mol^{-1} , due to the fact that the methyl rotors being some what similar to those in hydrocarbons, are freely rotating and hence has barriers below 3 kcal mol^{-1} . The barrier energy of the S—S rotor in $\text{CH}_3\text{SS}=\text{O}$ is also less than 3 kcal mol^{-1} due to minimum interaction between the methyl group and the O atom of $\text{S}=\text{O}$. The potential energy barrier for the S—S rotor in CH_3SSOH , CH_2SSOH , and $\text{CH}_3\text{SS(=O)H}$ and the S—O rotor in CH_3SSOH and CH_2SSOH is greater than 3 kcal mol^{-1} at a dihedral angle of around 180° and 360° degrees, primarily due to the severe interaction between methyl group and the O atom.

2.3.6 $S^{\circ}298$ and $C_p^{\circ}(T)$

Entropy and heat capacity values from vibration, translation and rotation contributions are calculated using SMCPs and the Rotator program. The scaled vibrations and the moment of inertia are from the optimized geometries by B3LYP/6-31G(d,p). A separate internal rotor analysis was carried out prior to running the Rotator program. Refer Table 2.9 for calculated entropy and heat capacities.

Table 2.9 Entropy ($S^{\circ}_{(298)}$) and Heat Capacity $C_p(T)$

Species	S°_{298} cal mol ⁻¹ K ⁻¹	$C_p^{\circ}(T)$ (cal mol ⁻¹ K ⁻¹)						
		300K	400K	500K	600K	800K	1000K	1500K
CH ₃ SSOH	74.26	20.58	23.51	25.93	27.91	30.93	33.20	36.93
<i>*I.R. Contribution</i>								
H-C—S-S	5.407	1.574	1.376	1.259	1.186	1.107	1.068	1.027
Total	79.67	22.15	24.87	27.19	29.10	32.04	34.27	37.96
CH ₃ SS(=O)H	73.03	17.85	21.11	23.92	26.24	29.81	32.40	36.34
<i>*I.R. Contribution</i>								
H-C—S-S	4.952	2.030	1.813	1.620	1.47	1.297	1.199	1.090
Total	77.982	19.88	22.92	25.54	27.72	31.11	33.60	37.43
•CH ₂ SSOH	74.27	21.24	23.81	25.61	26.92	28.81	30.21	32.64
<i>I.R. Contribution</i>								
S-S—C-H	4.6247	1.51	1.48	1.41	1.35	1.25	1.18	1.09
Total	78.89	22.75	25.29	27.02	28.27	30.06	31.39	33.73
CH ₃ SS•=O	70.01	18.31	20.84	22.85	24.46	26.88	28.68	31.62
<i>I.R. Contribution</i>								
H-C—S-S	5.727	1.06	1.03	1.02	1.01	1.00	1.00	1.00
C-S—S-O	5.613	2.27	2.30	2.16	1.98	1.68	1.48	1.23
Total	81.35	21.64	24.17	26.03	27.45	29.56	31.16	33.85

* *I.R. contribution is contribution to S°_{298} and $C_p^{\circ}(T)$ from internal rotations of the species around the central bond*

2.4 Summary

Thermochemical parameters are studied using density functional, ab initio and composite methods in computational chemistry. Enthalpies of formation for CH_3SSOH , $\text{CH}_3\text{SS(=O)H}$, $\text{CH}_3\text{SS:=O}$ and $\cdot\text{CH}_2\text{SSOH}$ are -38.46 (± 0.2) kcal mol^{-1} , -17.74 (± 0.2) kcal mol^{-1} , -17.02 (± 0.2) kcal mol^{-1} and 7.17 (± 0.2) kcal mol^{-1} respectively.

The C—H bond energy of $\text{H—CH}_2\text{SSOH}$, [$\text{CH}_3\text{SSOH-} [(\text{H}\cdot + \cdot\text{CH}_2\text{SSOH})]$] is 97.73 kcal mol^{-1} . The O—H bond energy of $\text{CH}_3\text{SSO—H}$ [$\text{CH}_3\text{SSOH-} [(\text{H}\cdot + \text{CH}_3\text{SS}\cdot\text{=O})]$] is 73.54 kcal mol^{-1} and in the bond cleavage, the dissociation results in immediate electron re-arrangement to form a sulfur – double bond to the O atom with the radical on the S atom. Similarly, the C—H bond in $\text{CH}_3\text{SS(=O)H}$, [$\text{CH}_3\text{SS(=O)H-} [(\text{H}\cdot + \cdot\text{CH}_2\text{SSOH})]$] is 77.01 kcal mol^{-1} . The S—H bond energy of $\text{CH}_3\text{SS(=O)H}$, [$\text{CH}_3\text{SS(=O)H-} [(\text{H}\cdot + \text{CH}_3\text{SS}\cdot\text{=O})]$] is 52.82 kcal mol^{-1} and the bond cleavage results in immediate electron re-arrangement to form a sulfur – double bond to the O atom with the radical on the S atom.

CHAPTER 3

STRUCTURAL AND THERMOCHEMICAL STUDIES ON THE S-S-O BRIDGED SYSTEM IN HSSOH AND HSS(=O)H AND RADICALS CORRESPONDING TO LOSS OF H ATOM

3.1 Introduction

Pyrolysis and mild oxidation of sulfur hydrocarbons is observed in collaborative studies to form solids, presumably higher molecular weight sulfur compounds or polymers through coupling of thiyl radicals form RS—S' bonds [Ref(1a) Xin Zeng, E. Fisher, F. Gouldin and J. W. Bozzelli , Proceedings 5th Joint US Combustion Institute Meeting, Sandiego, Calif, kinetics – 2007. 1b. Xin Zeng, E. Fisher, F. Gouldin and J. W. Bozzelli , Proceedings Eastern States US Combustion Institute Meeting, Charlottesville, Va, kinetics - October 2007.] Sulfur chemistry is also important in atmospheric climate change because both naturally occurring and anthropogenically emitted sulfur compounds form particulate and aerosols in the atmosphere that can reflect solar and absorb infrared radiation. They also affect production of atmospheric haze, acid rain, and may effect ozone depletion and sulfur oxide particles may also act as condensation nuclei for water vapor and enhance global cloudiness. In order to understand this sulfur coupling and to include it in models of sulfur oxidation. aerosol formation, or combustion, it is of value to know the thermochemistry of these hydrocarbons and oxy-hydrocarbons with the –S—S-O linkage.

The primary natural sources of sulfur oxides are volcanic emissions and oxidation of sulfur, the hydrocarbon's - methane thiol and dimethylsulfide, which are produced by in the biosphere and by oceanic phytoplankton. Human impact on the sulfur cycle is primarily in the production of sulfur dioxide (SO₂) from industry (e.g. burning coal) and the internal combustion engine. Sulfur dioxide can precipitate onto surfaces where it can

be oxidized to sulfate in the soil (it is also toxic to some plants), reduced to sulfide in the atmosphere, or oxidized to sulfate in the atmosphere as sulfuric acid, a principal component of acid rain [2]. With the rapid rise of economic development, acid rain has become one of the ten most serious problems which threaten the world environment [3].

The rich inventory of sulfur compounds containing hydrogen and oxygen atoms display only a few known $[\text{H}, \text{S}_n, \text{O}]^{0/+/-}$ [24]. The HSO and SOH radicals and their cations and anions are the well known, most simple species of this family [23]. Adams et al. suggested the existence of the SSOH radical as a neutral product of the reaction of S_2^+ some organic acids and alcohols [25]. However, with $n=2$, only the cation has been observed on a few occasions as a fragment in mass spectra of sulfur species [5].

As a continuation of our interest in sulfur rich compounds, in this paper we have studied the structure, bond energies, internal rotor potentials and the thermochemical properties of the di-sulfur compounds viz. oxatrisulfane (HSSOH) and its reactions to radicals, $\text{HSS}^*\text{=O}$ and $^*\text{SSOH}$ from loss of H is desirable to help in understanding its effect on environment.

Previous studies

It is widely regarded that oxy acids of sulfur compounds, where sulfur is in one of its lower oxidation states (sulfur can have coordination of 2, 4, or 6) such as isomers of $\text{R}_2\text{S}_2\text{O}$ or RHS_2O have low stability(s1) and we do not know of any compound of composition $\text{H}_2\text{S}_2\text{O}$ being reported. There are however reports of thiosulfinates, RS(=O)SR where HS(=O)SH would be a direct corresponding structure from hydrogen substitution for the organic (R) derivative(s)(s2). These RS(=O)SR compounds are sometimes termed thiol-sulfinates and disulfane oxides. The thermochemistry of the

species $\text{H}_2\text{S}_2\text{O}$, HRS_2O and $\text{R}_2\text{S}_2\text{O}$ have not been previously studied however there are ab initio calculations at the HF and MP2 levels for $\text{H}_2\text{S}_2\text{O}$ and $\text{Me}_2\text{S}_2\text{O}$ (references Strudel et al J. Phys Chem (1995) p 5319-26, s3, s4, s5). These studies present some relative energies of structures and project vibration frequencies for possible use in identification should they be synthesized.

There are even fewer studies on oxygenated radicals of the disulfide compounds with only the more simple $\text{HS}^*(=\text{O})$ and S^*OH radicals and their cations and anions somewhat well known [24, 23]. Adams et al. have studied the $^*\text{SSOH}$ radical as a possible neutral product of the reaction of S_2^+ with some organic acids and alcohols [25], where this cation has been observed on a few occasions as a fragment in mass spectra of sulfur species [26]. de Petris et al [22] have studied relative energies and structures of the $\text{HSS}^*(=\text{O})$ and HOSS^* radicals.

In this work we have studied the structure, bond energies, internal rotor potentials and the thermochemical properties of the di-sulfur compounds viz. hydroxyl disulfane (also termed oxatrisulfane) (HSSOH) and hydrogen dithiosulfanate ($\text{HSS}(=\text{O})\text{H}$) plus the radicals $\text{HSS}^*(=\text{O})$ and $^*\text{SSOH}$ and $^*\text{SS}(=\text{O})\text{H}$ which are formed via loss of H atom from the is desirable to help in understanding its effect on environment. Our enthalpy results are in reasonable agreement with previous calculated relative energy values.

3.2 Calculation Methods

The structure and thermochemical parameters of HSSOH are based on the density functional and composite ab initio levels using Gaussian 03 [6]. Computation levels include B3LYP/6-31G(d,p), B3LYP/6-311++G(3df,2p). The CBS-QB3 methods are utilized for improved enthalpies and bond energy analysis.

The enthalpies of formation for stable species are calculated using the total energies at B3LYP/6-31G(d,p), B3LYP/6-311++G(3df,2p), and CBS-QB3 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 [7] 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. The accuracy benefit from use of work reactions can also be observed in the good agreement of the DFT results with those of the higher level CBSQB3.

Contributions to $S^{\circ}298$ and $Cp^{\circ}(T)$ of each species are calculated using the “SMCPS” program [8], which incorporates the frequencies, moments of inertia, mass, symmetry, number of optical isomers, from the Gaussian calculation. Torsion frequencies are omitted in the SMCPS [8] calculation, and the “ROTATOR” program [8-10] is used for contributions from internal rotations that are less than 3.0 kcal to $S^{\circ}298$ and $Cp^{\circ}(T)$.

3.3 Results and Discussions

3.3.1 Structure

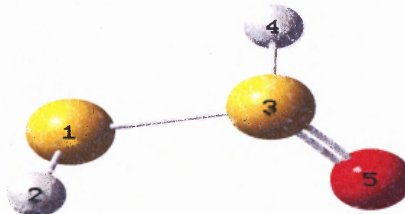
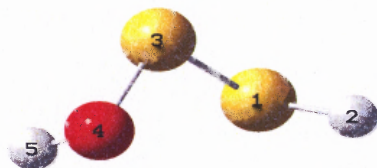
Structure information for the stable molecules is listed in Table 3.1 with illustrations. The S—S bond distances in HSSOH, HSS(=O)H and HSS^{*}=O are 2.07 Å, 2.2 Å and 2.15 Å respectively. The lowest energy structure for the individual species has been confirmed by comparing the lowest energy dihedral from the internal rotational potential curve with the structural parameter obtained from B3LYP/6-31G(d,p) of the parent molecule as shown in Table 3.2.

The S—O bond in HSSOH and ^{*}SSOH is 1.69Å, while S—O bond distance in HSS^{*}=O exhibits a shorter bond length of 1.51Å. In HSS(=O)H, the S—O bond is also similar to HSS^{*}=O at 1.49Å. The shorter S--O bond of 1.51Å of in HSS^{*}=O and HSS(=O)H is indicative of the double bond.

Table 3.1 Angles and bond distances from optimized Geometry using B3LYP/6-31G(d,p)

HSSOH

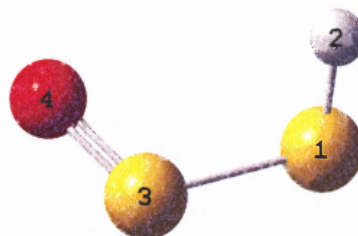
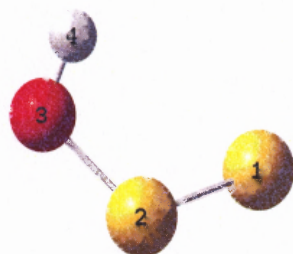
HSS(=O)H



R1	R(1,2)	1.355
R2	R(1,3)	2.074
R3	R(3,4)	1.687
R4	R(4,5)	0.970
A1	A(2,1,3)	99.89
A2	A(1,3,4)	106.15
A3	A(3,4,5)	106.89
D1	D(2,1,3,4)	-84.01
D2	D(1,3,4,5)	-85.50

R1	R(1,2)	1.349
R2	R(1,3)	2.199
R3	R(3,4)	1.387
R4	R(3,5)	1.492
A1	A(2,1,3)	93.70
A2	A(1,3,4)	85.34
A3	A(1,3,5)	114.05
A4	A(4,3,5)	108.74
D1	D(2,1,3,4)	-164.28
D2	D(2,1,3,5)	87.26

Table 3.1 continued

 **\cdot SSOH**

R1	R(1,2)	1.955
R2	R(2,3)	1.687
R3	R(3,4)	0.973
A1	A(1,2,3)	110.13
A2	A(2,3,4)	108.55
D1	D(1,2,3,4)	-50.53

HSS*(=O)

R1	R(1,2)	1.352
R2	R(1,3)	2.149
R3	R(3,4)	1.515
A1	A(2,1,3)	95.99
A2	A(1,3,4)	110.66
D1	D(2,1,3,4)	64.63

Table 3.2 Comparison of Lowest Energy Dihedral from PE Curve with Structural Parameter (see Figures 3.1 to 3.5)

Species	Potential curve	Structural Parameter	Dihedral
HSSOH	Figure 1	D1 D(2,1,3,4)	-84.01
	Figure 2	D2 D(1,3,4,5)	-85.50
·SSOH	Figure 3	D1 D(1,2,3,4)	-50.53
HSS·=O	Figure 4	D1 D(2,1,3,4)	64.63
HSS(=O)H	Figure 5	D2 D(2,1,3,5)	87.26

Table 3.3 refers to the Mulliken atomic charges for the molecules and their radicals. The S—S and S—O bonds in HSSOH, HSS(=O)H, ·SSOH, and in HSS·=O are all polar covalent bonds. However the degree of polarity is in the order of S=O > S—O > S—S.

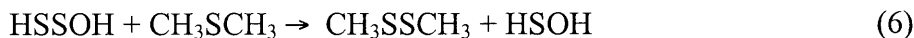
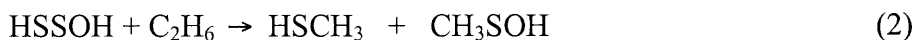
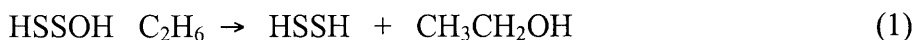
Table 3.3 Mulliken atomic charges for the molecules and their derived radicals

HSSOH		HSS(=O)H		HSS [•] =O		[•] SSOH	
Atoms	Charges	Atoms	Charges	Atoms	Charges	Atoms	Charges
1 S	-0.096	1 S	-0.165	1 S	-0.135	1 S	-0.159
2 H	0.088	2 H	0.090	2 H	0.098	2 S	0.369
3 S	0.225	3 S	0.574	3 S	0.455	3 O	-0.550
4 O	-0.556	4 H	0.018	4 O	-0.417	4 H	0.339
5 H	0.338	5 O	-0.518				

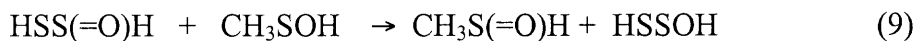
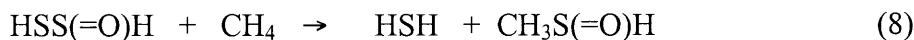
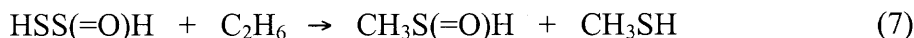
3.3.2 Heats of Formation and Enthalpies of Reaction

The following work reactions are used to calculate the heat of reaction and enthalpies of formation for HSSOH and HSS(=O)H molecule and their two radicals, HSS[•]=O and [•]SSOH respectively. The enthalpy calculations are based on the lowest energy conformer.

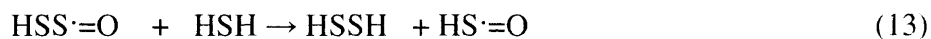
Work reactions for HSSOH:



Work reactions for HSS(=O)H:



Work reactions for HSS[•]=O:



Work reactions for $\cdot\text{SSOH}$

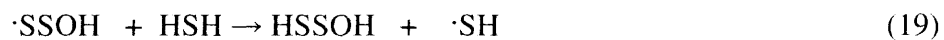
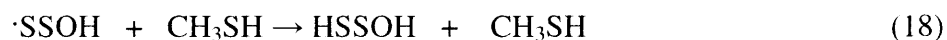
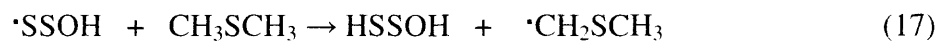
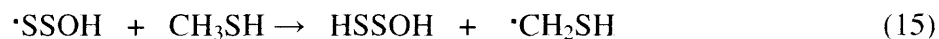


Table 3.4 compares the enthalpies of reaction for the above reactions; one can readily see the similarity in the reaction energies from the different work reactions. It is interesting to note that larger basis set in the B3LYP calculations does not always result in better agreement with the CBS-QB3 value.

Table 3.4 Calculated $\Delta H_{\text{rxn}(298)}$ (kcal mol⁻¹) from isodesmic reactions

Isodesmic reaction	B3LYP/6-311G (d, p)	B3LYP/6-311G (3df, 2p)	CBSQB3
<i>Work reactions for HSSOH:</i>			
HSSOH + C ₂ H ₆ → HSSH + CH ₃ CH ₂ OH	-2.48	-0.848	0.966
HSSOH + C ₂ H ₆ → HSCH ₃ + CH ₃ SOH	11.24	12.93	11.86
HSSOH + CH ₄ → HSH + CH ₃ SOH	9.98	11.32	10.11
HSSOH + CH ₃ SH → CH ₃ SSH + HSOH	15.79	16.05	9.69
HSSOH + HSH → HSSH + HSOH	19.23	19.35	19.35
HSSOH + CH ₃ SCH ₃ → CH ₃ SSCH ₃ + HSOH	14.87	14.69	13.62
<i>Work reactions for HSS(=O)H:</i>			
HSS(=O)H + C ₂ H ₆ → CH ₃ S(=O)H + CH ₃ SH	5.64	7.27	6.27
HSS(=O)H + CH ₄ → HSH + CH ₃ S(=O)H	4.38	5.66	4.52
HSS(=O)H + CH ₃ OH → CH ₃ S(=O)H + HSOH	-5.59	-5.65	-5.58
<i>Work reactions for HSS=O:</i>			
HSS=O + CH ₃ OH → HSSOH + CH ₃ O·	24.77	30.17	34.35
HSS=O + C ₂ H ₅ OH → HSSOH + C ₂ H ₅ O·	26.89	32.43	33.83
HSS=O + CH ₃ SOH → HSSOH + CH ₃ S·=O	-6.19	-5.94	-5.50
HSS=O + HSH → HSSH + HS·=O	16.99	24.25	17.85
HSS=O + CH ₃ SCH ₃ → CH ₃ SSCH ₃ + HS·=O	12.63	19.59	12.12
<i>Work reactions for ·SSOH</i>			
·SSOH + CH ₃ SH → HSSOH + ·CH ₂ SH	30.27	28.15	29.32
·SSOH + C ₂ H ₅ SH → HSSOH + CH ₃ ·CHSH	27.38	25.91	27.83
·SSOH + CH ₃ SCH ₃ → HSSOH + ·CH ₂ SCH ₃	29.07	23.63	28.37
·SSOH + CH ₃ SH → HSSOH + CH ₃ SH	17.40	19.65	20.78
·SSOH + HSH → HSSOH + ·SH	22.53	-24.54	25.53

Table 3.5 compares the heat of formation for the Species under study using various levels of calculations. Overall there is very good agreement in the $\Delta H_f(298)$ values across the calculation methods and down the work reactions. Similar calculations were also run for the reference species whose literature values are listed in table 5.

Table 3.5 Calculated Enthalpies of formation (kcal mol⁻¹) of species in isodesmic work reaction

Isodesmic reaction	B3LYP/6-31G(d,p)	B3LYP/6-311G(3df,2p)	CBSQB3
<i>Enthalpies of Formation of HSSOH:</i>			
HSSOH + C ₂ H ₆ → HSSH + CH ₃ CH ₂ OH	-28.85	-30.49	-32.30
HSSOH + C ₂ H ₆ → HSCH ₃ + CH ₃ SOH	-29.80	-31.49	-30.43
HSSOH + CH ₄ → HSH + CH ₃ SOH	-30.88	-32.23	-31.02
HSSOH + CH ₃ SH → CH ₃ SSH + HSOH	-38.76	-39.02	-32.66
HSSOH + HSH → HSSH + HSOH	-37.55	-37.68	-37.67
HSSOH + CH ₃ SCH ₃ → CH ₃ SSCH ₃ + HSOH	-38.88	-38.70	-37.63
Average	-34.12	-34.94	-33.62
<i>Mean of averages</i>	-34.23		
<i>Enthalpies of Formation of HSS(=O)H:</i>			
HSS(=O)H + C ₂ H ₆ → CH ₃ S(=O)H + CH ₃ SH	-10.91	-12.54	-11.54
HSS(=O)H + CH ₄ → HSH + CH ₃ S(=O)H	-11.99	-13.27	-12.13
HSS(=O)H + CH ₃ SOH → CH ₃ S(=O)H + HSSOH	-14.98	-14.93	-14.99
Average	-12.62	-13.58	-12.88
<i>Mean of averages</i>	-13.03		
<i>Enthalpies of Formation of HSS=O:</i>			
HSS=O + CH ₃ OH → HSSOH + CH ₃ O·	-6.52	-11.91	-16.09
HSS=O + C ₂ H ₅ OH → HSSOH + C ₂ H ₅ O·	-8.56	-14.09	-15.44
HSS=O + CH ₃ SOH → HSSOH + CH ₃ S=O	-12.09	-12.35	-12.78
HSS=O + HSH → HSSH + HS=O	-13.12	-20.37	-13.97
HSS=O + CH ₃ SCH ₃ → CH ₃ SSCH ₃ + HS=O	-14.44	-21.40	-13.93
Average	-10.94	-16.02	-14.44
<i>Mean of averages*</i>	-15.23		

*only include B3LYP/6-311G(3df,2p) and CBSQB3 in the mean.

Table 3.5 continued

Isodesmic reaction	B3LYP/6-31G(d,p)	B3LYP/6-311G(3df,2p)	CBSQB3
Enthalpies of Formation of \cdotSSOH			
\cdot SSOH + CH ₃ SH \rightarrow HSSOH + \cdot CH ₂ SH	-20.97	-18.86	-20.03
\cdot SSOH + C ₂ H ₅ SH \rightarrow HSSOH + CH ₃ \cdot CHSH	-19.59	-18.12	-20.04
\cdot SSOH + CH ₃ SCH ₃ \rightarrow HSSOH + \cdot CH ₂ SCH ₃	-20.23	-17.79	-19.24
\cdot SSOH + CH ₃ SH \rightarrow HSSOH + CH ₃ SH	-15.91	-18.16	-19.29
\cdot SSOH + HSH \rightarrow HSSOH + \cdot SH	-16.31	-17.76	-21.21
Average	-18.60	-18.13	-19.96
Mean of averages		-18.90	

Table 3.6 lists the enthalpy values of reference species and the literature reference for each.

Table 3.6 Enthalpies of formation (in kcal mol⁻¹) of reference species in work reactions

Species	ΔH_{f298}°	Species	ΔH_{f298}°
H [11]	52.1	C ₂ H ₆ [17]	-20.04
CH ₄ [16]	-17.89	HSSH [28]	3.98
CH ₃ SCH ₃ [11]	-8.94	CH ₃ SH [20]	-5.47
C ₂ H ₅ OH [19]	-56.17	CH ₃ SOH [14]	-33.9
C ₂ H ₅ SH [12]	-10.99	CH ₃ OH [19]	-48.04
\cdot CH ₂ SCH ₃ [12]	33.78	CH ₃ \cdot CHSH	30.64
\cdot CH ₂ SH [13]	37.7	CH ₃ SO \cdot [13]	18.31
C ₂ H ₅ O \cdot [28]	-3.9	CH ₃ O \cdot [18]	4.1
CH ₃ S(=O)H [21]	-20.6	HSH [22]	-4.9
HSOH [22]	-27.2	CH ₃ O \cdot [28]	4.1
HS \cdot =O [28]	-5.0	CH ₃ SSCH ₃ [28]	-5.75
HS \cdot [22]	33.3	HSSOH [this work]	-33.62

Of the above three methods, used in the calculation of enthalpies of formation of several species, B3LYP/6-31G(d,p) did not give satisfactory results due to smaller basis set. The results of B3LYP/6-311++G(3df,2p) are closer to CBS-QB3 composite method. Since we obtain very good agreement with the CBS-QB3 method for all of the work reactions and as the composite CBS-QB3 method has an advantage of utilizing geometry and frequencies calculated at the same level of theory, the CBS-QB3 composite method is recommended for thermo chemical determination on these S-S bridge systems.

3.3.3 Bond Energies

The Bond Energy of S—H bond in HSSOH is calculated using [HSSOH- [(H• + •SSOH)]] reaction and the bond energy of O—H in HSSOH is calculated using [HSSOH- [(H• + HSSO•)]]. Similarly, the Bond Energy of S—H bond in H—SS(=O)H is calculated using [HSS(=O)H- [(H• + •SSOH)]] reaction and the bond energy of S—H in HSS(O)—H is calculated using [HSS(=O)H- [(H• + HSS•=O)]] as shown in Table 3.7.

Table 3.7 Bond energy calculation in kcal/mole

Bond Energy for	B3LYP/6-311G(d,p)	B3LYP/6-311G(3df,2p)	CBSQB3	Average
HSSOH:				
S-H bond	-71.29	-68.91	-65.76	- 68.65
O-H bond	-75.28	-71.02	- 71.28	- 72.52
HSS(=O)H:				
S-H bond (H—SS(O)H)	-49.79	-47.37	-45.02	- 47.39
S-H bond (HSS(O)—H)	-53.78	-49.66	-50.54	- 51.33

**average Hf values from table 2 have been used to calculate the bond energy*

Thus the Bond Energy of S—H bond in HSSOH is 65.76 kcal mol⁻¹. And the bond energy of O—H in HSSOH is 71.28 kcal mol⁻¹. Thus the O—H bond is stronger than S—H bond in HSSOH. Similarly, the S—H bond in H—SS (=O) H is 45.02 kcal mol⁻¹. And the bond energy of S—H in HSS (=O) —H is 50.54 kcal mol⁻¹.

3.3.4 Frequencies and Moment of Inertia

The frequencies and the moment of inertia are used to calculate the thermochemical properties entropy and heat capacity as a function of temperature from the formulas for these properties developed using statistical mechanics (ref benson, thermochemical kinetics john wiley and son 1976). The list of the frequencies and the moments of inertia of the parent molecules and the corresponding radicals are listed in Table 3.8.

Table 3.8 Frequencies and moments of inertia

Species	Moment of Inertia, units $\text{amu}(\text{Bohr})^2$			frequencies (cm^{-1})		
	<i>I</i> 1	<i>I</i> 2	<i>I</i> 3	<i>a</i>	<i>a</i>	<i>a</i>
HSSOH	87.93381	423.37242	493.34687	260.579	397.881	460.475
				488.944	739.108	884.907
				1198.369	2627.330	3761.611
HSS(=O)H	68.52238	462.34677	507.06404	252.672	293.297	408.500
				710.846	970.726	1079.582
				1139.184	2353.112	2685.627
SSOH	73.90734	386.61948	457.28657	113.768	289.140	619.197
				(716.891)	1138.732	3740.530
HSS [*] =O	65.36502	427.18318	482.59420	134.712	(279.480)	(436.801)
				779.147	1054.774	2657.625

**Frequencies in bold corresponds to torsions that are removed in the SMCPs Analysis*

3.3.5 Internal Rotation Potential

The stable molecule HSSOH has two internal rotators (HS—SOH and HSS—OH) and barriers to both rotors are high and have two fold or near twofold symmetry. The two barriers for HS—SOH rotation are 11.5 and 10.5, while the two barriers for HSS-OH are both 7.7 kcal mol⁻¹.

The corresponding radicals $\cdot\text{SSOH}$ and $\text{HSS}\cdot=\text{O}$ have only one rotor each, $\cdot\text{SS—OH}$ and HS—S(=O)H . The internal rotors in these disulfide molecules are more similar to those in hydrocarbons with barriers near and below 3 kcal mol^{-1} . The $\cdot\text{SS—OH}$ rotor has only one barrier at 2.45 with a second very small barrier at $0.1 \text{ kcal mol}^{-1}$. The HS—S(=O)H rotor has two fold potential with barriers are 1.75 and $0.8 \text{ kcal mol}^{-1}$.

Torsion frequencies are used for contributions to entropy and heat capacity from rotors with energy barriers significantly greater than 3 kcal mol^{-1} . Rotations about The $\text{HS—S}\cdot=\text{O}$ rotor and $\cdot\text{SS—OH}$ rotor have energy barriers less than $3.0 \text{ kcal mol}^{-1}$ and contributions to these internal rotors are calculated with Rotator program [8-10], and values substituted in place of the value determined from the torsion frequency estimate.

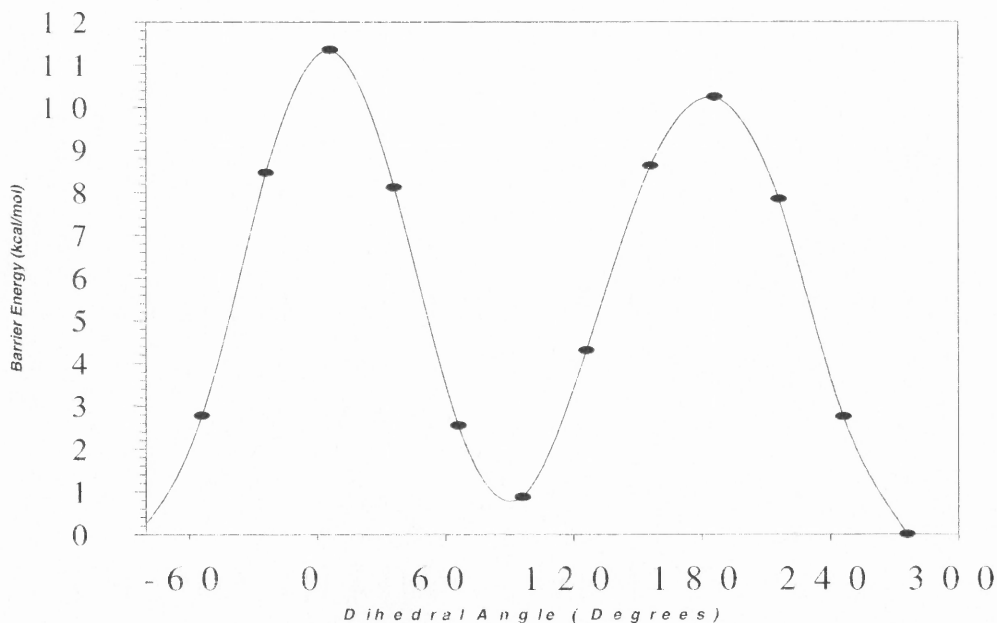


Figure 3.1 Potential energy profile for the HS—SOH) rotor in HSSOH molecule

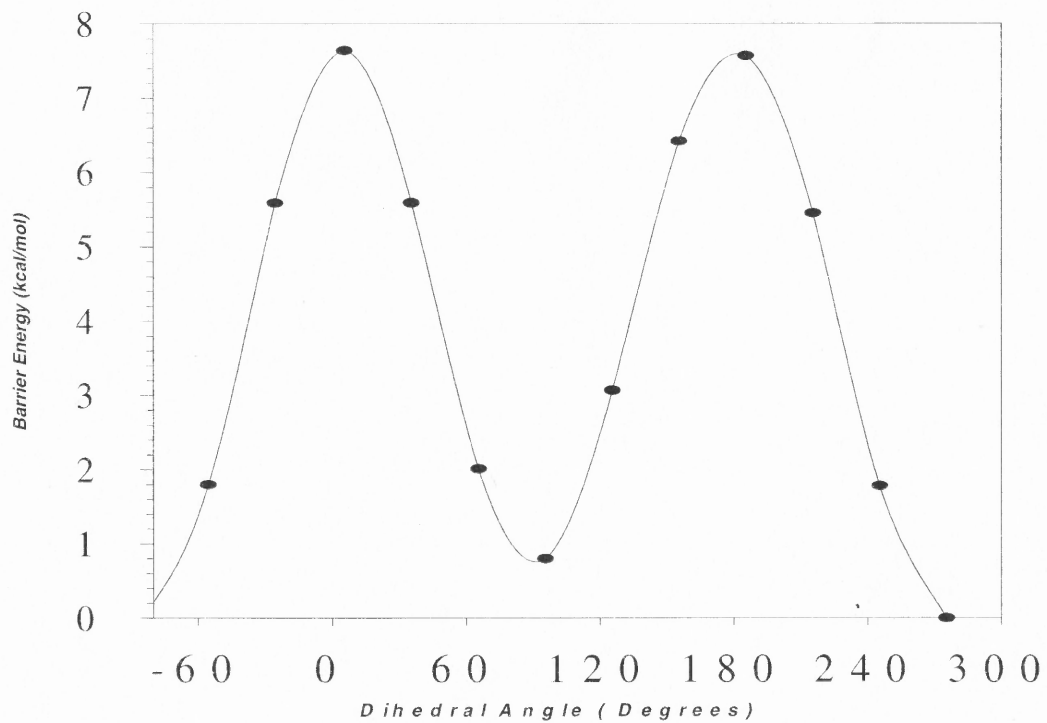


Figure 3.2 Potential energy profile for the HSS—OH rotor in HSSOH molecule

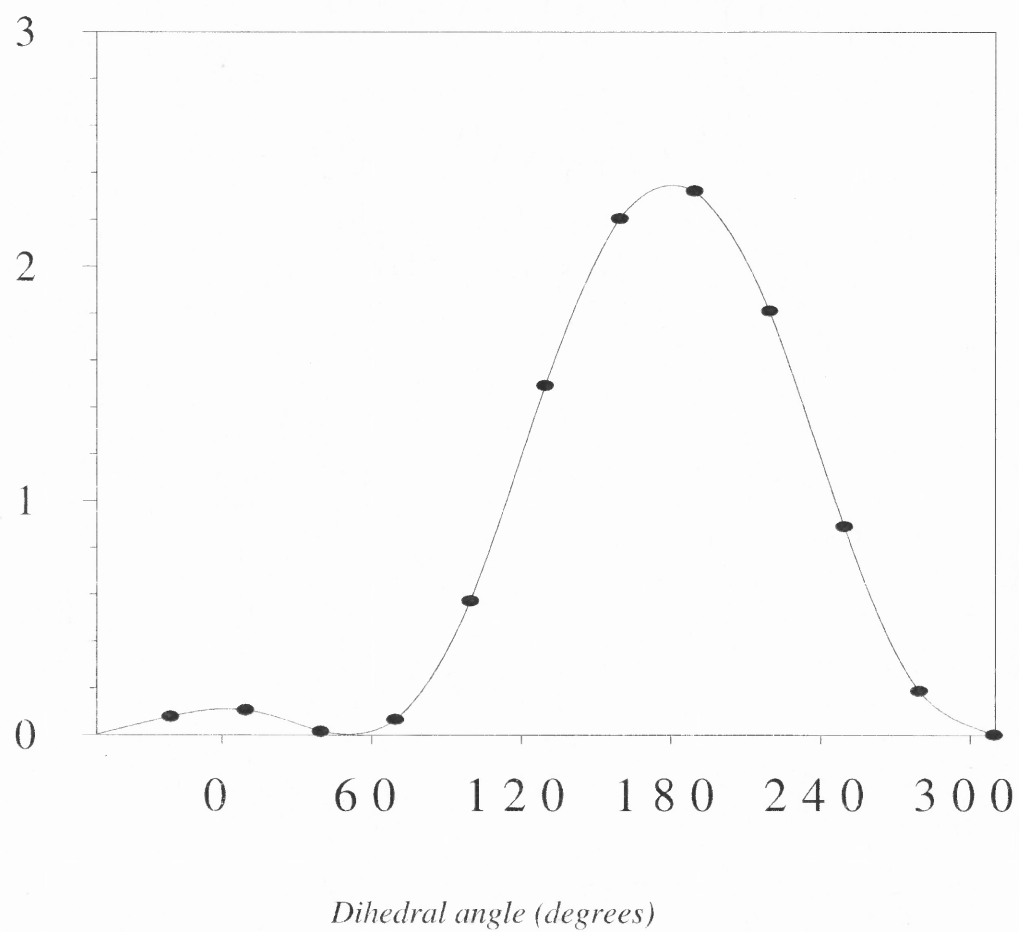


Figure 3.3 Potential energy profile for S-S—O-H rotor in 'SSOH molecule

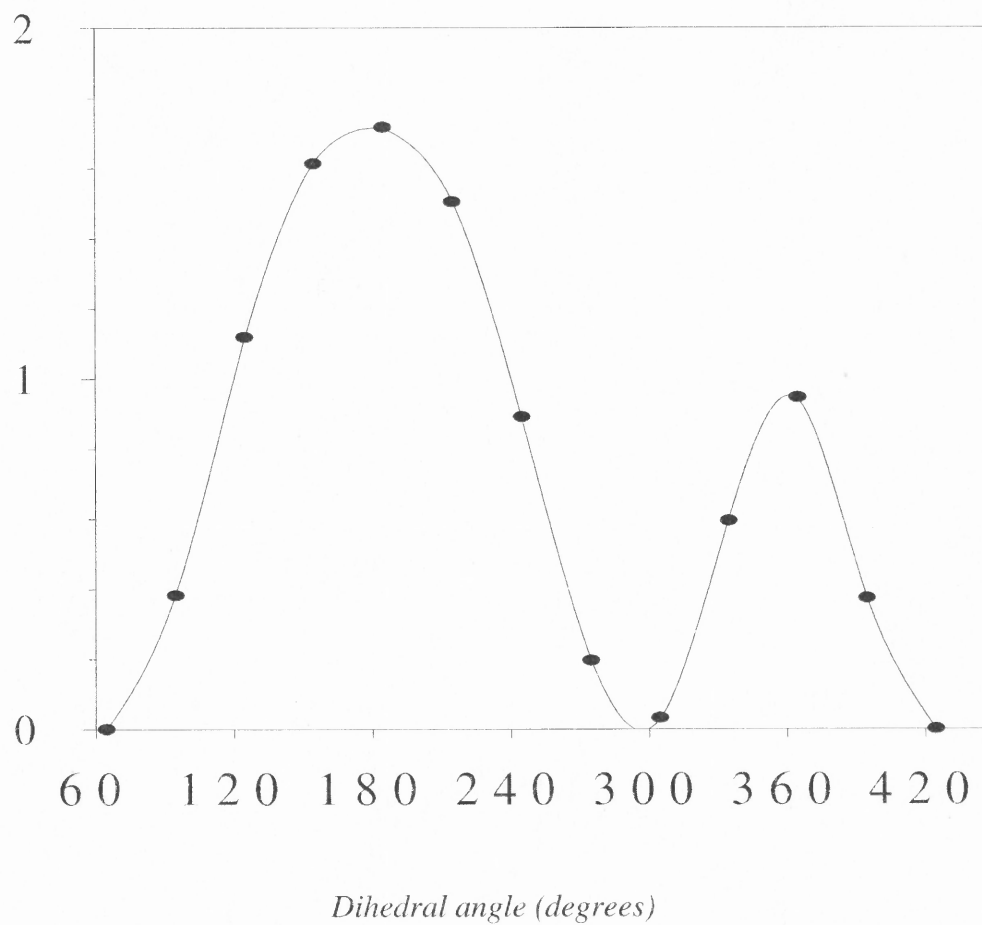


Figure 3.4 Potential energy profile for the HS—S'O rotor in H-SS'O

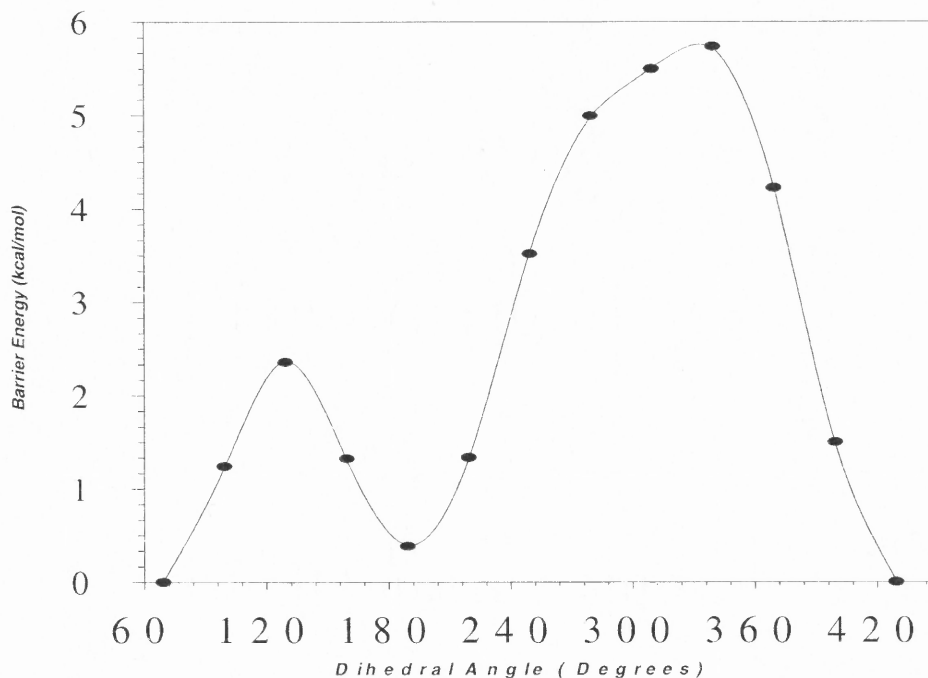


Figure 3.5 Potential energy profile for the H-S—S(=O)H rotor in HSS(=O)H molecule

The barrier energy of the S—S rotor in HSSOH and HSS(=O)H and the S—O in HSSOH is greater than 3 kcal mol^{-1} primarily due to greater level of interaction between the O and H atom. The barriers for the S—S rotors in HSS.=O and S—O in .SSOH are lower than 3 kcal mol^{-1} .

3.3.6 $S^{\circ}298$ and $C_p^{\circ}(T)$

Entropy and heat capacity values from vibration, translation and rotation contributions are calculated using SMCPS and the Rotator program. The scaled vibrations and the moment of inertia are from the optimized geometries by B3LYP/6-31G(d,p). Entropy

and $C_p(T)$ parameters from the internal rotor analysis was carried using “Rotator” program [8-10]. Refer table 3.9 for calculated entropy and heat capacities.

Table 3.9 Entropy ($S^\circ_{(298)}$) and Heat Capacity $C_p(T)$

Species	S°_{298} cal mol ⁻¹ K ⁻¹	$C_p^\circ(T)$ (cal mol ⁻¹ K ⁻¹)						
		300K	400K	500K	600K	800K	1000K	1500K
HSSOH	66.41	13.57	15.34	16.58	17.50	18.81	19.76	21.32
<i>*I.R Contribution</i>								
None	-----	-----	-----	-----	-----	-----	-----	-----
Total	66.41	13.57	15.34	16.58	17.50	18.81	19.76	21.32
HSS(=O)H	66.31	12.90	14.66	16.06	17.19	18.88	20.06	21.77
<i>*I.R Contribution</i>								
None	-----	-----	-----	-----	-----	-----	-----	-----
Total	66.31	12.90	14.66	16.06	17.19	18.88	20.06	21.77
•SSOH	66.78	11.71	12.85	13.65	14.21	14.95	15.45	16.32
<i>I.R Contribution</i>								
S-S—O-H	3.39	2.19	1.98	1.77	1.61	1.39	1.27	1.12
Total	70.17	13.9	14.83	15.42	15.82	16.34	16.72	17.44
HSS•=O	67.24	12.09	13.16	13.94	14.51	15.35	15.94	16.80
<i>I.R Contribution</i>								
H-S—S-S	3.20	1.61	1.50	1.39	1.30	1.19	1.13	1.06
Total	70.44	13.7	14.66	15.33	15.81	16.54	17.07	17.86

* *I.R contribution is contribution to S°_{298} and $C_p^\circ(T)$ from internal rotations of the species around the central bond.*

3.4 Summary

Thermochemical parameters are studied using density functional, and ab initio composite methods in computational chemistry. Enthalpies of formation for HSSOH, HSS(=O)H, HSS=O and \cdot SSOH are -33.62 (± 0.2) kcal mol^{-1} , -12.88 (± 0.2) kcal mol^{-1} , -14.44 (± 0.2) kcal mol^{-1} and -19.96 (± 0.2) kcal mol^{-1} respectively. The S—H Bond Energy of HSSOH is 65.76 kcal mol^{-1} , and the O—H bond energy is 71.28 kcal mol^{-1} . The O—H bond results because the HSSOH parent undergoes electron re-arrangement upon loss of the HSSO—H hydrogen atom to form the more stable HSS \cdot =O structure. The S—H Bond Energy of H—SS(=O)H is weak at only 45.02 kcal mol^{-1} and results in the formation of \cdot SSOH radical by the loss of hydrogen atom, and the S-H bond energy of HSS(=O)—H is very weak at 50.54 kcal mol^{-1} . The very weak S—H bond, upon loss of the HSS(=O)—H hydrogen atom forms a more stable HSS \cdot =O radical.

CHAPTER 4

STRUCTURAL AND THERMOCHEMICAL STUDIES ON S-S-O BRIDGED SYSTEM IN $\text{CH}_3\text{SSOCH}_3$ AND RADICALS CORRESPONDING TO LOSS OF H ATOM

4.1 Introduction

Methyl Mercaptan (CH_3SH), dimethyl sulfide (DMS; CH_3SCH_3), dimethyl disulfide (DMDS; CH_3SSCH_3) are the most abundant reduced sulfur compounds in the atmosphere as well as dominant sulfur species in the troposphere released by biogenic sources. Because these compounds are highly reactive in the gas phase, ultimately leading to sulfate, their decomposition has been studied extensively in experimental and field services [27].

The reaction of methylthiyl radical ($\text{CH}_3\text{S}\cdot$) with $^3\text{O}_2$ is a potentially important process for both combustion and atmospheric chemistry as a pathway for the exothermic conversion (oxidation) of, CH_3S . This reaction system also serves as a surrogate reaction system for a number of paths in longer chain and substituted thiol radical reactions with molecular oxygen [3]. This $\text{CH}_3\text{S} + \text{O}_2 \leftrightarrow \text{CH}_3\text{S-OO}$ reaction has a very shallow well, $\sim 10 \text{ kcal mol}^{-1}$, which results in a very rapid reverse reaction to back to $\text{CH}_3\text{S}\cdot$ and a quasi equilibrium. The CH_3S and CH_3SOO can react with hydroperoxides (e.g. HO_2 , $\text{CH}_3\text{SOO}\cdot$) or OH or NO_x to form the CH_3SO moiety, which exists as $\text{CH}_3\text{S}\cdot(=\text{O})$.

$\text{CH}_3\text{S}\cdot(=\text{O})$ has been postulated as one of the key intermediates in the DMS oxidation mechanism. It may play an important role in the formation of acid rain because the bond length of the C—S bond is longer than that in CH_3S . The principal mechanism

of SO₂ formation has been suggested to include a sequence of reactions of the CH₃S•=O radical with O₂, NO₂, and O₃ as well as the thermal decomposition of CH₃-SO₂ [5].

It has been shown that the CH₃SS•=O radical can be formed by the reaction CH₃SS + NO₂ → CH₃SS•=O + NO and CH₃SS•=O can potentially react with NO₂ to give several products [15]. Until now, however, there has been no theoretical or experimental study on the stability and thermochemical properties of CH₃SSOCH₃ and its radicals. Thus, a detailed knowledge about structure, bond energies, internal rotor potentials and the thermochemical properties of the di sulfur methyl thiols and its reactions to radicals from loss of H is desirable to help in understanding its effect on environment.

In the studies undertaken below it has been observed that one of the radicals of CH₃SSOCH₃, namely CH₃SSOC•H₂ falls apart upon rotating its internal rotors as seen through Gauss view. Hence this radical may not exist.

4.2 Calculation Method

The structure and thermochemical parameters of $\text{CH}_3\text{SSOCH}_3$ are based on the density functional and composite ab initio levels using Gaussian 03 [6]. Computation levels include B3LYP/6-31G(d,p), B3LYP/6-311++G(3df,2p). The CBS-QB3 methods are utilized for improved energies and analysis.

The enthalpies of formation for stable species are calculated using the total energies at B3LYP/6-31G(d,p), B3LYP/6-311++G(3df,2p), and CBS-QB3 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 [7] 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 PE diagram. Contributions to S°_{298} and $C_p^\circ(T)$ of each species are calculated using the "SMCPS" program [8] which incorporates the frequencies, moments of inertia, mass, symmetry, number of optical isomers, from the Gaussian calculation. It also incorporates frequency corrections. Torsion frequencies are omitted in SMCPS [8] calculation, and the "ROTATOR" program [8-10] is used for contributions from internal rotations that are less than 3.0 kcal to S°_{298} and $C_p^\circ(T)$.

4.3 Results and Discussion

4.3.1 Structure

The S—O bond distance in CH₃SSOCH₃ is 1.69 Å and 1.68 Å in ¹CH₂SSOCH₃ and 1.71 Å in CH₃SSOC¹H₂.

The C—S bond in CH₃SSOCH₃ and CH₃SSOC¹H₂ is 1.83 Å against the 1.73 Å in ¹CH₂SSOCH₃. The C—O bond distance in CH₃SSOCH₃ and ¹CH₂SSOCH₃ is 1.43 Å and 1.36 Å, slightly shorter in CH₃SSOC¹H₂.

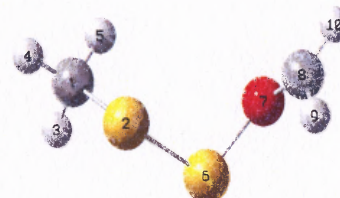
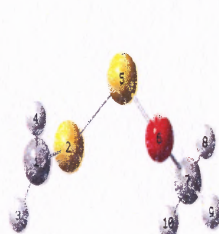
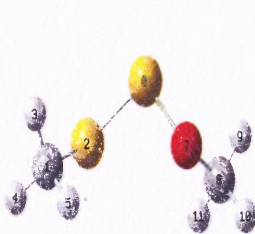
The formation of ¹CH₂SSOCH₃ is accompanied by reduction of the O-C-H bond angle to 107.15°, while formation of CH₃SSOC¹H₂ reveals increase in bond angle O-C-H to 118.90° compared to the O-C-H bond angle of 111.47° in CH₃SSOCH₃ as listed in Table 4.1.

Table 4.1 Angles and bond distances from optimized Geometry using B3LYP/6-31++G(d,p)

CH₃SSOCH₃

·CH₂SSOCH₃

CH₃SSOC·H₂



R(1,2)	1.839	R(1,2)	1.728	R(1,2)	1.83
R(1,3)	1.090	R(1,3)	1.08	R(1,3)	1.09
R(1,4)	1.093	R(1,4)	1.08	R(1,4)	1.09
R(1,5)	1.090	R(2,5)	2.09	R(1,5)	1.09
R(2,6)	2.060	R(5,6)	1.68	R(2,6)	2.05
R(6,7)	1.690	R(6,7)	1.43	R(6,7)	1.71
R(7,8)	1.433	R(7,8)	1.09	R(7,8)	1.36
R(8,9)	1.095	R(7,9)	1.09	R(8,9)	1.08
R(8,10)	1.093	R(7,10)	1.09	R(8,10)	1.08
R(8,11)	1.096	A(2,1,3)	117.61	A(2,1,3)	110.66
R(9,10)	1.790	A(2,1,4)	120.94	A(2,1,4)	106.20
R(10,11)	1.785	A(3,1,4)	121.43	A(2,1,5)	110.13
A(2,1,3)	110.5	A(1,2,5)	105.37	A(3,1,4)	109.69
A(2,1,4)	106.37	A(2,5,6)	107.17	A(3,1,5)	110.53
A(2,1,5)	110.12	A(5,6,7)	114.90	A(4,1,5)	109.50

Table 4.1 continued

A(3,1,4)	109.69	A(6,7,8)	111.45	A(1,2,6)	103.87
A(3,1,5)	110.45	A(6,7,9)	105.66	A(2,6,7)	107.15
A(4,1,5)	109.56	A(6,7,10)	111.01	A(6,7,8)	116.41
A(1,2,6)	103.67	A(8,7,9)	109.82	A(7,8,9)	118.90
A(2,6,7)	106.59	A(8,7,10)	109.48	A(7,8,10)	112.86
A(6,7,8)	114.70	A(9,7,10)	109.31	A(9,8,10)	123.04
A(7,8,9)	111.47	D(3,1,2,5)	-149.49	D(3,1,2,6)	58.40
A(7,8,10)	105.75	D(4,1,2,5)	29.84	D(4,1,2,6)	177.39
A(7,8,11)	111.07	D(1,2,5,6)	79.35	D(5,1,2,6)	-64.11
A(9,8,11)	109.44	D(2,5,6,7)	80.84	D(1,2,6,7)	82.45
A(9,10,11)	60.05	D(5,6,7,8)	55.36	D(2,6,7,8)	75.97
D(3,1,2,6)	58.99	D(5,6,7,9)	174.62	D(6,7,8,9)	29.19
D(4,1,2,6)	178.01	D(5,6,7,10)	-66.97	D(6,7,8,10)	-175.47
D(5,1,2,6)	-63.33				
D(1,2,6,7)	81.49				
D(2,6,7,8)	80.44				
D(6,7,8,9)	55.85				
D(6,7,8,10)	175.07				
D8 D(6,7,8,11)	-66.48				

The lowest energy structure for the individual species has been confirmed by comparing the lowest energy dihedral from the internal rotational potential curve with the structural parameter obtained from B3LYP/6-31G(d,p) of the parent molecule as shown in Table 4.2. And Table 4.3 refers to the Mulliken atomic charges for the molecules and their radicals

Table 4.2 Comparison of Lowest Energy Dihedral from PE Curve with Structural Parameter (see Figures 4.1 to 4.8)

Table			
Species	Potential curve	Structural Parameter	Dihedral
CH ₃ SSOCH ₃			
	Figure 1	D(3,1,2,6)	58.99
		D(4,1,2,6)	178.01
	Figure 2	D(1,2,6,7)	81.49
	Figure 3	D(6,7,8,9)	55.85
		D(6,7,8,10)	175.07
	Figure 4	D(2,6,7,8)	80.44
·CH ₂ SSO CH ₃			
	Figure 5	D(4,1,2,5)	29.84
	Figure 6	D(1,2,5,6)	79.35
	Figure 7	D(2,5,6,7)	80.84
	Figure 8	D(5,6,7,8)	55.36
		D(5,6,7,9)	174.62

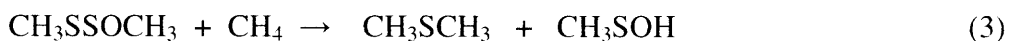
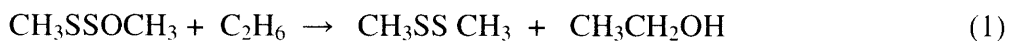
Table 4.3 Mulliken atomic charges for the molecules and their derived radicals

CH ₃ SSOCH ₃		·CH ₂ SSOCH ₃	
Atoms	Charges	Atoms	Charges
1 C	-0.464197	1 C	-0.383294
2 S	0.009295	2 S	0.073155
3 H	0.156638	3 H	0.149426
4 H	0.147390	4 H	0.157543
5 H	0.161376	5 S	0.220501
6 S	0.221644	6 O	-0.512072
7 O	-0.521316	7 C	-0.073593
8 C	-0.072791	8 H	0.117289
9 H	0.114968	9 H	0.129337
10 H	0.125708	10 H	0.121709
11 H	0.121284		

4.3.2 Heats of Formation and Enthalpies of Reaction

The following work reactions are used to calculate the heat of reaction and enthalpies of formation for $\text{CH}_3\text{SSOCH}_3$ and its radical, $\cdot\text{CH}_2\text{SSOCH}_3$. The enthalpy calculations are based on the lowest energy conformer.

Work reactions $\text{CH}_3\text{SSOCH}_3$:



Work reactions for $\cdot\text{CH}_2\text{SSOCH}_3$:

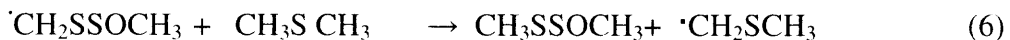
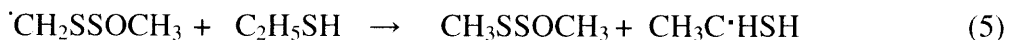


Table 4.4 illustrates the comparative study on enthalpies of reaction for the above reactions. Table 4.5 compares the heat of formation for the Species under study using various levels of calculations. Similar calculations were also run for the reference species whose literature values are listed in table 4.6.

Table 4.4 Calculated $\Delta H_{\text{rxn}298}$ (kcal mol⁻¹) from isodesmic reactions

Isodesmic reaction	B3LYP/6-31G (d, p)	B3LYP/6-311++G (3df, 2p)	CBSQB3
<i>Work reactions for CH₃SSOCH₃:</i>			
CH ₃ SSOCH ₃ + C ₂ H ₆ → CH ₃ SS CH ₃ + CH ₃ CH ₂ OH	-8.11	-7.77	-6.20
CH ₃ SSOCH ₃ + C ₂ H ₆ → CH ₃ SC ₂ H ₅ + CH ₃ SOH	6.96	6.99	5.41
CH ₃ SSOCH ₃ + CH ₄ → CH ₃ S CH ₃ + CH ₃ SOH	8.71	9.06	8.67
<i>Work reactions for ·CH₂SSOCH₃ :</i>			
·CH ₂ SSOCH ₃ + CH ₃ SH → CH ₃ SSOCH ₃ + ·CH ₂ SH	- 1.32	-1.82	-2.33
·CH ₂ SSOCH ₃ + C ₂ H ₅ SH → CH ₃ SSOCH ₃ + CH ₃ C·HSH	-4.21	-4.06	-3.82
·CH ₂ SSOCH ₃ + CH ₃ S CH ₃ → CH ₃ SSOCH ₃ + ·CH ₂ SCH ₃	-2.52	-3.34	-3.58

Table 4.5 Calculated Enthalpies of formation (kcal mol⁻¹) of species in isodesmic work reaction

Isodesmic reaction	B3LYP/6-31G(d,p)	B3LYP/6-311++G(3df,2p)	CBSQB3
<i>Enthalpies of Formation of CH₃SSOCH₃:</i>			
CH ₃ SSOCH ₃ + C ₂ H ₆ → CH ₃ SS CH ₃ + CH ₃ CH ₂ OH	-32.97	-33.31	-35.68
CH ₃ SSOCH ₃ + C ₂ H ₆ → CH ₃ SC ₂ H ₅ + CH ₃ SOH	-34.48	-34.51	-33.69
CH ₃ SSOCH ₃ + CH ₄ → CH ₃ S CH ₃ + CH ₃ SOH	-33.66	-34.01	-33.62
Average	-33.70	-33.94	-34.33
<i>Mean of averages</i>	-33.99		
<i>Enthalpies of Formation of ·CH₂SSOCH₃ :</i>			
·CH ₂ SSOCH ₃ + CH ₃ SH → CH ₃ SSOCH ₃ + ·CH ₂ SH	10.79	11.05	11.17
·CH ₂ SSOCH ₃ + C ₂ H ₅ SH → CH ₃ SSOCH ₃ + CH ₃ C·HSH	12.18	11.78	11.16
·CH ₂ SSOCH ₃ + CH ₃ S CH ₃ → CH ₃ SSOCH ₃ + ·CH ₂ SCH ₃	11.54	12.12	11.97
Average	11.50	11.65	11.44
<i>Mean of averages</i>	11.53		

Table 4.6 Enthalpies of formation (in kcal mol⁻¹) of reference species in work reactions

Species	ΔH_{f298}°	Species	ΔH_{f298}°
H [11]	52.1	C ₂ H ₆ [17]	-20.04
CH ₄ [16]	-17.89	CH ₃ SCH ₃ [11]	-8.94
CH ₃ SH [20]	-5.47	C ₂ H ₅ OH [19]	-56.17
CH ₃ SOH [14]	-33.9	C ₂ H ₅ SH [12]	-10.99
CH ₃ OH [19]	-48.04	\cdot CH ₂ SCH ₃ [12]	33.78
CH ₃ \cdot CHSH [28]	30.64	\cdot CH ₂ SH [3]	37.7
CH ₃ SSOCH ₃ [this work]	-34.33		

Since we obtain very good agreement with the CBS-QB3 method for all of the work reactions and as the composite CBS-QB3 method has an advantage of utilizing geometry and frequencies calculated at the same level of theory, the CBS-QB3 composite method is recommended for thermo chemical determination on these S-S-Obridge systems.

4.3.3 Bond Energies

The Bond Energy of C—H bond in H—CH₂SSOCH₃ is calculated using [CH₃SSOCH₃-[(H· + ·CH₂SSOCH₃)]] reaction as shown in Table 4.7.

Table 4.7 Bond energy calculation in kcal/mole.

Bond Energy for	B3LYP/6-311G(d,p)	B3LYP/6-311G(3df,2p)	CBSQB3	Average
<i>CH₃SSOCH₃:</i>				
C-H bond	-97.3	-97.69	-97.87	-97.62

**average Hf values from table 2 have been used to calculate the bond energy*

4.3.4 Frequencies and Moment of Inertia

The frequencies and the moment of inertia help to identify the species using spectroscopic methods like FTIR. The list of the frequencies and the moments of inertia of the parent molecules and the corresponding radicals are listed in Table 4.8.

Table 4.8 Frequencies and moment of inertia

Species	Moment of Inertia, units $\text{amu}(\text{Bohr})^2$			frequencies (cm^{-1})					
	<i>I</i> 1	<i>I</i> 2	<i>I</i> 3	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
CH ₃ SSOCH ₃	301.07941	1024.63242	1059.36895	79.6	117.7	128.6	173.6	216.3	307.3
				390.0	488.1	672.5	680.4	978.2	982.0
				1024.1	1172.7	1191.7	1360.5	1471.1	474.9
				1491.3	1493.4	1513.5	3028.4	3065.1	3103.0
				3135.0	3159.0	3177.2			
•CH ₂ SSOCH ₃	185.80059	654.61197	711.35111	78.1	115.8	154.3	199.8	217.6	306.6
				381.2	402.3	454.1	676.5	786.8	934.3
				1020.5	1172.4	1190.4	1410.7	1471.6	1493.2
				1511.1	3030.6	3106.0	3138.6	3168.7	3302.0

4.3.5 Internal Rotational Potential

The parent CH₃SSOCH₃ and corresponding methyl radical •CH₂SSOCH₃ has four internal rotors. While CH₃SSOC•H₂ falls apart to CH₃S=O while rotating the S—O rotor. In these disulfide molecules we find the methyl rotors are somewhat similar to those in hydrocarbons with barriers near and below 3 kcal mol⁻¹, and the CS—SO and CSS-OR rotors have barriers near 5 kcal mol⁻¹ or higher. In our entropy analysis, rotors with energy barriers greater than 3.0 kcal are not included in entropy and heat capacity calculations. Rotations about the H₃C—SS and SO—CH₃ bond in CH₃SSOCH₃, the H₃C—SS and SO—CH₃ bonds in •CH₂SSOCH₃, have energy barriers less than 3.0 kcal.

used instead of the contribution from the torsion frequency estimation in the Gaussian calculation.

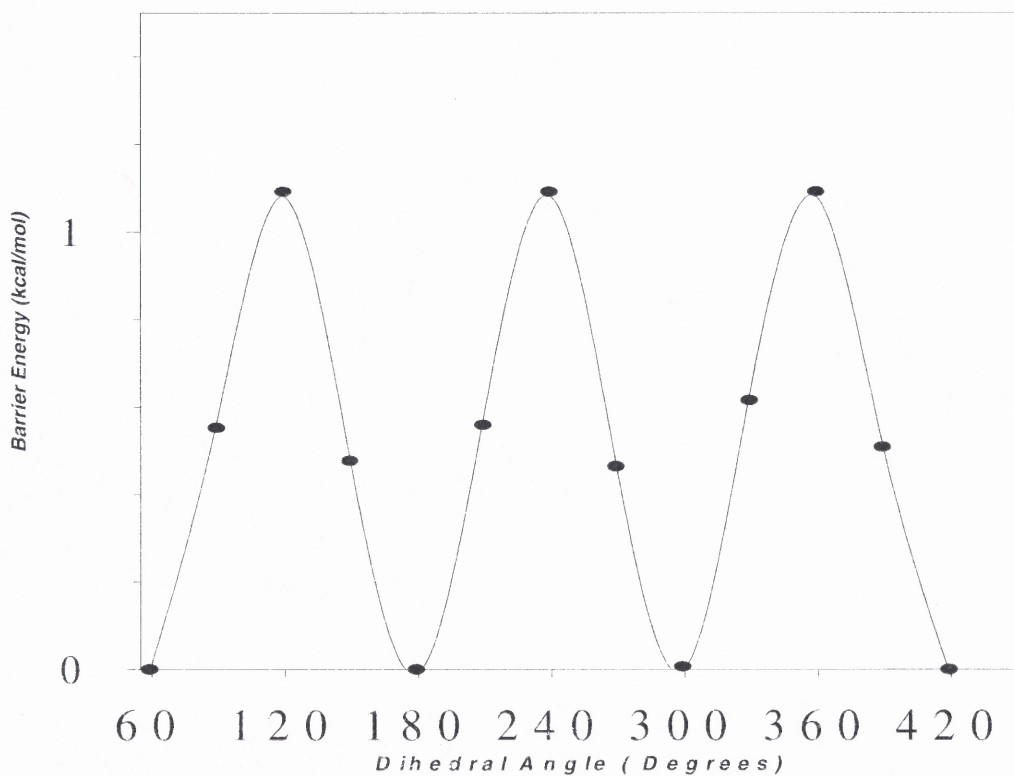


Figure 4.1 Potential energy profile for the H-C—S-(SOC) rotor in CH₃SSOCH₃ molecule

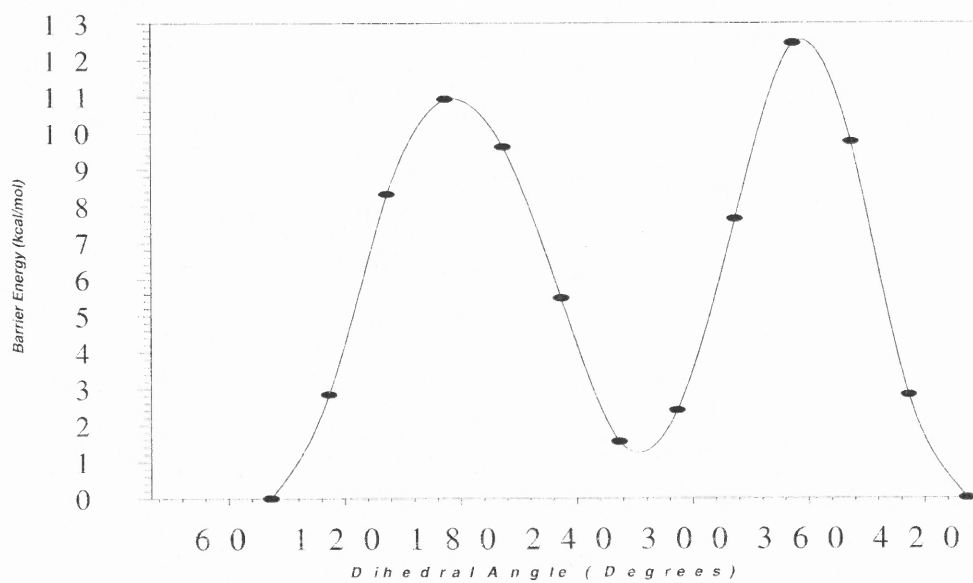


Figure 4.2 Potential energy profile for the (CH₃)S—S(OH) rotor in CH₃SSOCH₃H molecule

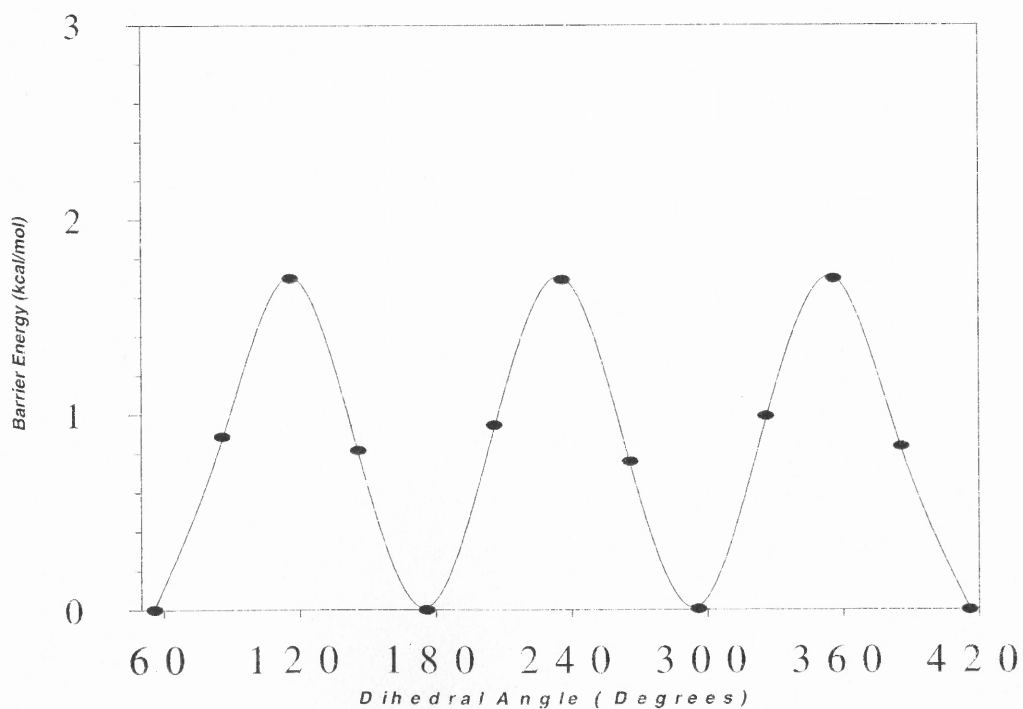


Figure 4.3 Potential energy profile for the (CH₃SS O—C) rotor in CH₃SSOCH₃ molecule

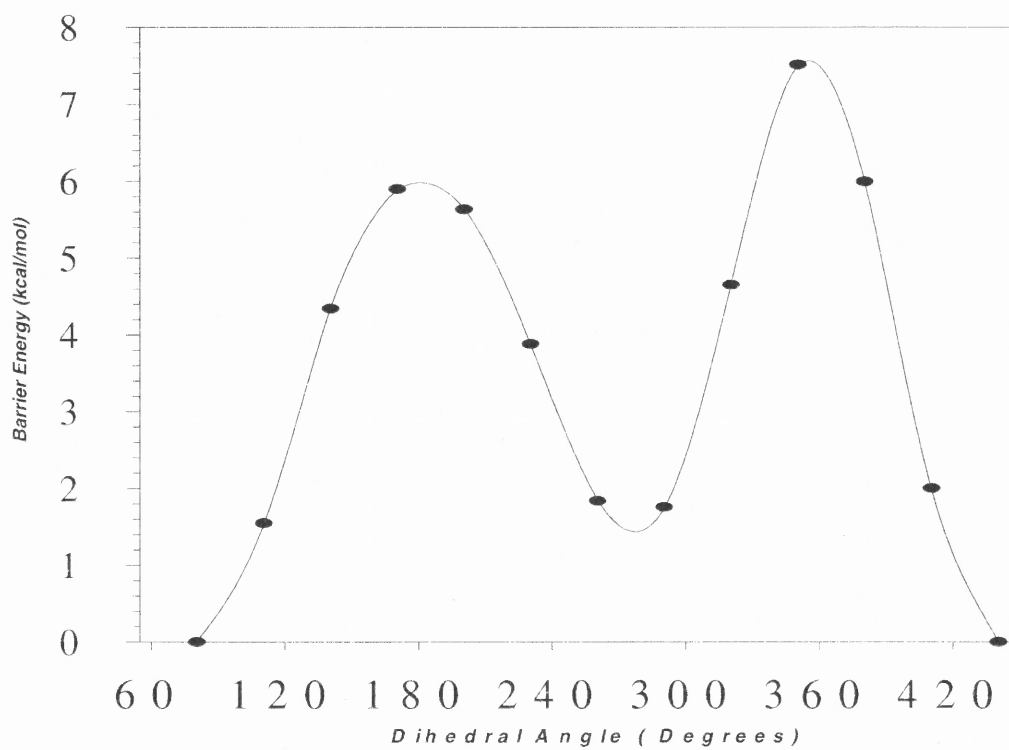


Figure 4.4 Potential energy profile for CH₃S(S—OC) rotor in CH₃SSOCH₃ molecule

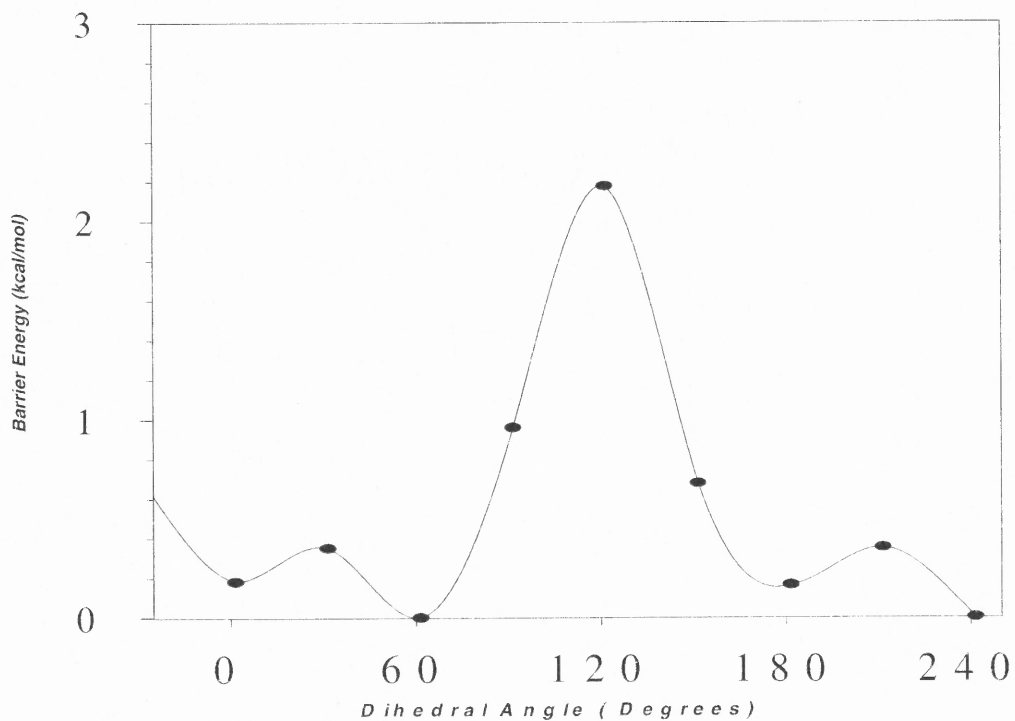


Figure 4.5 Potential energy profile for C—S rotor in $\text{CH}_2\text{-SSOC}$ molecule

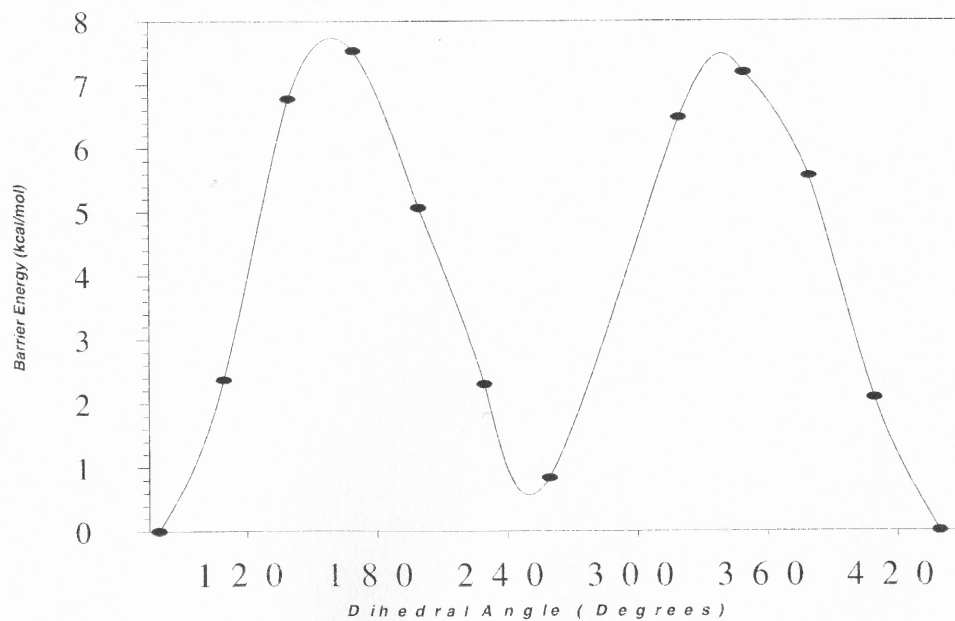


Figure 4.6 Potential energy profile for the $^{\circ}\text{CH}_2\text{S—SO—C}$ rotor in $^{\circ}\text{CH}_2\text{SSOCH}_3$ molecule

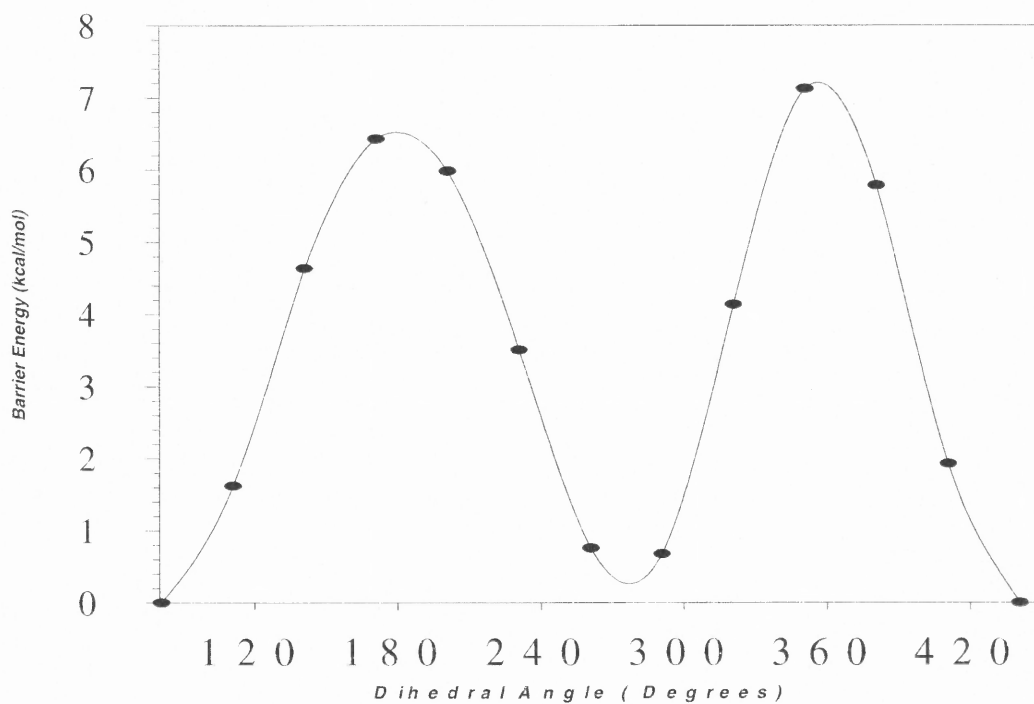


Figure 4.7- Potential energy profile for the $^{\circ}\text{CH}_2\text{S(S—OC)}$ rotor in $^{\circ}\text{CH}_2\text{SSOCH}_3$ molecule

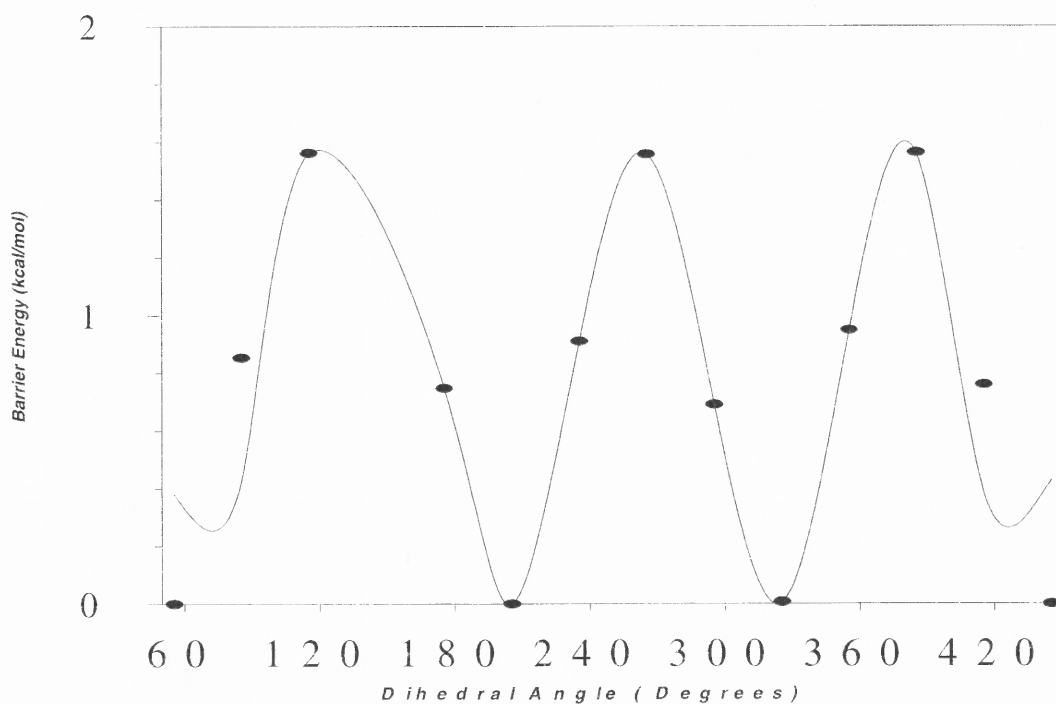


Figure 4.8 Potential energy profile for the 'CH₂-SSO—C rotor in 'CH₂SSOCH₃ molecule

The C—S and C—O rotors studied so far has the barrier near and below 3 kcal mol⁻¹, due to the fact that the methyl rotors being some what similar to those in hydrocarbons are freely rotating and hence has barriers below 3 kcal mol⁻¹. The potential energy barrier for the S—S rotor and S—O rotor in CH₃SSOCH₃ and 'CH₂SSOCH₃ is greater than 3 kcal mol⁻¹ at dihedral angle of around 180° and 360 degrees, primarily due to the severe interaction between methyl group and the O atom.

4.3.6 $S^{\circ}298$ and $C_p^{\circ}(T)$

Entropy and heat capacity values from vibration, translation and rotation contributions are calculated using SMCPs and the Rotator program. The scaled vibrations and the moment of inertia are from the optimized geometries by B3LYP/6-31G(d,p). A separate internal rotor analysis was carried out prior to running the Rotator program. Refer Table 4.9 for calculated entropy and heat capacities.

Table 4.9 Entropy ($S^{\circ}_{(298)}$) and $C_p(T)$ and Heat Capacity

Species	$S^{\circ}298$ cal mol ⁻¹ K ⁻¹	$C_p^{\circ}(T)$ (cal mol ⁻¹ K ⁻¹)						
		300K	400K	500K	600K	800K	1000K	1500K
CH ₃ SSOCH ₃	78.80	21.93	26.30	30.19	33.51	38.74	42.66	48.83
<i>*I.R Contribution</i>								
H-C—S-S	5.43	1.55	1.35	1.245	1.176	1.101	1.064	1.02
S-O—CH	5.074	1.93	1.70	1.52	1.39	1.23	1.15	1.07
Total	89.30	25.41	29.35	32.95	36.07	41.07	44.87	50.92
•CH ₂ SSOCH ₃	75.49	18.98	22.69	25.84	28.46	32.55	35.61	40.51
<i>I.R Contribution</i>								
S-S—C-H	4.781	1.46	1.37	1.30	1.24	1.16	1.11	1.05
S-O—CH	5.09	1.94	1.69	1.50	1.37	1.22	1.15	1.06
Total	85.36	22.38	25.75	28.64	31.07	34.93	37.87	42.62

* *I.R contribution is contribution to $S^{\circ}298$ and $C_p^{\circ}(T)$ from internal rotations of the species around the central bond.*

4.4 Summary

Thermochemical parameters are studied using density functional, and ab initio composite methods in computational chemistry. Enthalpies of formation for $\text{CH}_3\text{SSOCH}_3$ and $\bullet\text{CH}_2\text{SSOCH}_3$ are -34.33 (± 0.2) kcal mol^{-1} and 11.44 (± 0.2) kcal mol^{-1} respectively. The C—H bond energy of $\text{CH}_3\text{SSOCH}_3$ is 97.62 kcal mol^{-1} . In the studies undertaken below it has been observed that one of the radicals of $\text{CH}_3\text{SSOCH}_3$, namely $\text{CH}_3\text{SSOC}\cdot\text{H}_2$ falls apart upon rotating its internal rotors as seen through Gauss view. Hence this radical may not exist.

APPENDIX A

ADDITIONAL DATA ON ENTROPY

Additional entropy data for species presented in this thesis

Appendix A1 Entropy (S^0) Data for CH_3SSOH , $\text{CH}_3\text{SS(=O)H}$, $\cdot\text{CH}_2\text{SSOH}$ and $\text{CH}_3\text{SS}\cdot=\text{O}$

Species	$S^{\circ}298$ (cal mol ⁻¹ K ⁻¹)						
	500 K	1200 K	1500 K	2000 K	3000 K	4000 K	5000 K
CH_3SSOH	85.50	111.23	119.02	129.65	145.46	157.04	166.15
<i>*I.R Contribution</i>							
H-C—S-S	6.13	7.120	7.35	7.645	8.053	8.341	8.564
Total	91.63	118.35	126.37	137.29	153.51	165.38	174.71
$\text{CH}_3\text{SS(=O)H}$	83.74	109.39	117.28	128.03	143.96	155.60	164.74
<i>*I.R Contribution</i>							
H-C—S-S	6.15	7.072	8.54	7.628	8.042	8.311	8.508
Total	89.89	116.46	125.82	135.66	152.00	163.91	173.25
$\cdot\text{CH}_2\text{SSOH}$	85.64	109.52	116.41	125.70	139.38	149.35	157.18
<i>I.R Contribution</i>							
S-S—C-H	5.39	6.497	6.75	7.054	7.474	7.767	7.991
Total	91.03	116.02	123.16	132.75	146.85	157.12	165.17
$\text{CH}_3\text{SS}\cdot=\text{O}$	78.91	99.75	106.12	114.80	127.67	137.07	144.47
<i>I.R Contribution</i>							
H-C—S-S	6.26	7.145	7.37	7.654	8.057	8.343	8.565
C-S—S-O	6.79	8.304	8.59	8.928	9.369	9.669	9.897
Total	91.96	115.20	122.08	131.38	145.09	155.08	162.93

Appendix A2 Entropy (S°) Data for HSSOH, HSS(=O)H, 'SSOH and HSS'=O

Species	S°_{298} (cal mol ⁻¹ k ⁻¹)						
	2000 K	2500 K	3000 K	3500 K	4000 K	4500 K	5000 K
HSSOH	101.44	106.45	110.62	114.19	117.30	120.05	122.53
<i>*I.R Contribution</i>							
None	---	--	--	--	--	--	--
Total	101.44	106.45	110.62	114.19	117.30	120.05	122.53
HSS(=O)H	101.21	106.30	110.51	114.11	117.24	120.01	122.50
<i>*I.R Contribution</i>							
None	--	--	--	--	--	--	--
Total	101.21	106.30	110.51	114.11	117.24	120.01	122.50
'SSOH	94.68	98.47	101.62	104.30	106.64	108.71	110.57
<i>I.R Contribution</i>							
S-S—O-H	6.64	6.78	7.07	7.32	7.53	7.72	7.89
Total	101.32	105.25	108.69	111.62	114.17	116.43	118.46
HSS'=O	95.89	99.76	102.95	105.66	108.02	110.11	111.98
<i>I.R Contribution</i>							
H-S—S-O	5.59	5.82	6.00	6.16	6.29	6.41	6.52
Total	101.48	105.58	108.95	111.82	114.31	116.52	118.5

Appendix A3 Entropy (S^0) Data for $\text{CH}_3\text{SSOCH}_3$ and $\cdot\text{CH}_2\text{SSOCH}_3$

Species	$S^{\circ 298}$ (cal mol ⁻¹ k ⁻¹)						
	2000 K	2500 K	3000 K	3500 K	4000 K	4500 K	5000 K
$\text{CH}_3\text{SSOCH}_3$	150.51	162.32	172.24	180.75	188.20	194.82	200.77
<i>*I.R Contribution</i>							
HC-SS	7.65	7.88	8.06	8.21	8.35	8.46	8.57
SO-CH	7.63	7.86	8.04	8.20	8.33	8.45	8.56
Total	165.79	178.06	188.34	197.16	204.88	211.73	217.9
$\cdot\text{CH}_2\text{SSOCH}_3$	135.81	145.60	153.81	160.86	167.02	172.50	177.42
<i>*I.R Contribution</i>							
SS-CH	7.07	7.30	7.48	7.64	7.77	7.89	7.99
SO-CH	7.63	7.86	8.04	8.20	8.33	8.45	8.56
Total	150.51	160.76	169.33	176.70	183.12	188.84	193.97

APPENDIX B

ADDITIONAL DATA ON HEAT CAPACITIES

Additional data on heat capacities for species presented in this thesis

Appendix B1 Heat Capacity (Cp(T)) Data for CH₃SSOH, CH₃SS(=O)H, ¹CH₂SSOH and CH₃SS^{*}=O

Species	Cp ^o (T) (cal mol ⁻¹ K ⁻¹)					
	1200 K	1500 K	2000 K	3000 K	4000 K	5000 K
CH ₃ SSOH	33.91	35.89	37.95	39.84	40.62	41.00
<i>*I.R Contribution</i>						
H-C—S-S	1.046	1.027	1.013	1.002	0.998	0.996
Total	34.96	36.92	38.96	40.85	41.62	42.00
CH ₃ SS(=O)H	34.32	36.34	38.34	40.08	40.77	41.10
<i>*I.R Contribution</i>						
H-C—S-S	1.140	1.090	1.047	0.989	0.939	0.806
Total	35.46	37.44	39.39	41.07	41.71	41.91
¹ CH ₂ SSOH	30.21	31.55	32.99	34.37	34.94	35.23
<i>I.R Contribution</i>						
S-S—C-H	1.135	1.092	1.053	1.022	1.010	1.004
Total	31.34	32.64	34.04	35.39	35.95	36.23
CH ₃ SS [*] =O	27.71	29.33	0.95	32.39	32.97	33.25
<i>I.R Contribution</i>						
H-C—S-S	0.998	0.996	0.995	0.994	0.994	0.993
C-S—S-O	1.347	1.229	1.129	1.055	1.028	1.015
Total	30.06	31.55	33.08	34.44	34.99	35.26

Appendix B2 Heat Capacity (Cp(T)) Data for HSSOH, HSS(=O)H, 'SSOH and HSS'=O

Species	Cp°(T) (cal mol ⁻¹ K ⁻¹)						
	2000 K	2500 K	3000 K	3500 K	4000 K	4500 K	5000 K
HSSOH	22.19	22.70	23.01	23.22	23.35	23.45	23.52
<i>*I.R Contribution</i>							
None	--	--	--	--	--	--	---
Total	22.19	22.70	23.01	23.22	23.35	23.45	23.52
HSS(=O)H	22.57	22.99	23.24	23.39	23.49	23.56	23.62
<i>*I.R Contribution</i>							
None	--	--	--	--	--	---	--
Total	22.57	22.99	23.24	23.39	23.49	23.56	23.62
'SSOH	16.83	17.15	17.34	17.47	17.56	17.62	17.67
<i>I.R Contribution</i>							
S-S—C-H	1.02	1.00	1.00	1.00	1.00	1.00	1.00
Total	17.85	18.15	18.34	18.47	18.56	18.62	18.67
HSS'=O	17.21	17.43	17.56	17.64	17.70	17.73	17.76
<i>I.R Contribution</i>							
H-C—S-S	1.03	1.02	1.01	1.00	1.00	1.00	1.00
Total	18.24	18.45	18.57	18.64	18.70	18.73	18.76

Appendix B3 Heat Capacity (Cp(T)) Data for CH₃SSO CH₃ and [•]CH₂SSOH

Species	Cp ^o (T) (cal mol ⁻¹ K ⁻¹)						
	2000 K	2500 K	3000 K	3500 K	4000 K	4500 K	5000 K
CH ₃ SSO CH ₃	52.04	53.82	54.89	55.57	56.03	56.35	56.59
<i>*I.R Contribution</i>							
HC-SS	1.01	1.00	1.00	0.99	0.99	0.99	0.99
SO-CH	1.03	1.02	1.01	1.00	1.00	1.00	1.00
Total	54.08	55.84	56.90	57.56	58.02	58.34	58.58
[•] CH ₂ SSOH	43.11	44.56	45.44	46.00	46.37	46.64	46.83
<i>*I.R Contribution</i>							
SS-CH	1.03	1.01	1.01	1.00	1.00	1.00	1.00
SO-CH	1.03	1.02	1.01	1.00	1.00	1.00	1.00
Total	45.17	46.59	47.46	48.00	48.37	48.64	48.83

APPENDIX C
INPUT FILES FOR SMCPS

Input files to the program SMCPS for the species presented in this thesis

Appendix C1 Input file for CH₃SSOH

```

NAME (name of molecule)
Ch3ssoh

COMMENTS:
b3_631gdp

TEMPERATURE
14 (Number of temperature to be read in)
298 400 500 600 800 900 1000 1200 1500 2000 2500 3000 4000 5000

ROTOR
1 number of internal rotors

MOLECULAR WT
95.97036

OPTICAL ISOMER
1

MULTIPLICITY
1 multiplicity of molecular specie of interest

HF298
0

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1 H 4 S 2 O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

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

rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
!1 (include decimal input)

MOMENT (1)=10 e-40 g*cm^2 (2)=GHz (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3 choice of moment of inertia units
203.44971 664.79585 728.21371

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)
18
112.6426 139.4611 230.3880
279.2984 448.4174 496.2172
680.7653 721.9113 978.1456
983.6915 1189.1481 1361.0707
1475.0957 1491.7125 3065.2373
3159.1959 3177.8225 3763.8482

```

Appendix C2 Input file for CH₃SS(=O)H

NAME (name of molecule)
ch3ss(=o)h

COMMENTS:
b3_631gdp

TEMPERATURE
14 (Number of temperature to be read in)
298 400 500 600 800 900 1000 1200 1500 2000 2500 3000 4000 5000

ROTOR
1 number of internal rotors

MOLECULAR WT
95.97036

OPTICAL ISOMER
1

MULTIPLICITY
1 multiplicity of molecular specie of interest

HF298
0

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1 H 4 S 2 O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

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

rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
!1 (include decimal input)

MOMENT (1)=10 e-40 g*cm² (2)=GHz (3)=amu-Bohr² (4)=amu-Angstrom²
3 choice of moment of inertia units
217.27895 569.62069 725.95448

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm⁻¹)
18
99.7500 184.9095 204.8992
326.4873 405.7815 697.0727
831.0269 990.1809 996.8946
1076.0499 1100.6693 1368.3658
1484.7357 1498.8458 2350.2194
3050.7991 3144.4502 3166.7281

Appendix C3 Input file for •CH₂SSOH

```

NAME (name of molecule)
Ch2ssohR

COMMENTS:
b3_631gdp

TEMPERATURE
14 (Number of temperature to be read in)
298 400 500 600 800 900 1000 1200 1500 2000 2500 3000 4000 5000

ROTOR
1 number of internal rotors

MOLECULAR WT
94.96253

OPTICAL ISOMER
1

MULTIPLICITY
1 multiplicity of molecular specie of interest

HF298
0

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1 H 3 S 2 O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

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

rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, svib,
Cpvib)
!1 (include decimal input)

MOMENT (1)=10 e-40 g*cm^2 (2)=GHZ (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3 choice of moment of inertia units
185.80059 654.61197 711.35111

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)
15
116.1712 201.2926 221.0928
277.1666 400.9334 460.2321
467.7453 722.6752 787.1176
934.0427 1189.5832 1409.7102
3169.4933 3303.2677 3760.6083

```

Appendix C4 Input file for CH₃SS^{*}=O

```

NAME (name of molecule)
Ch3ssor

COMMENTS:
b3_631gdp

TEMPERATURE
14 (Number of temperature to be read in)
298 400 500 600 800 900 1000 1200 1500 2000 2500 3000 4000 5000

ROTOR
2 number of internal rotors

MOLECULAR WT
94.96253

OPTICAL ISOMER
1

MULTIPLICITY
1 multiplicity of molecular specie of interest

HF298
0

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1 H 3 S 2 O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

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

rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
!1 (include decimal input)

MOMENT (1)=10 e-40 g*cm^2 (2)=GHZ (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3 choice of moment of inertia units
211.85814 533.28842 720.50403

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)
15
51.2706 115.4289 221.0911
353.0535 436.4048 694.3697
982.2280 995.2895 1069.7198
1365.9187 1482.2376 1493.6876
3062.9128 3159.0875 3174.3031

```


Appendix C5 Input file for HSSOH

```

NAME (name of molecule)
hssoh

COMMENTS:
b3_631gdp

TEMPERATURE
15 (Number of temperature to be read in)
298 300 400 500 600 800 1000 1500 2000 2500 3000 3500 4000 4500 5000

ROTOR
1 number of internal rotors

MOLECULAR WT
81.95471

OPTICAL ISOMER
1

MULTIPLICITY
1 multiplicity of molecular specie of interest

HF298
0

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 0 H 2 S 2 O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

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

rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, svib,
Cpvib)
!1 (include decimal input)

MOMENT (1)=10 e-40 g*cm^2 (2)=GHZ (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3 choice of moment of inertia units
87.93381 423.37242 493.34687

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)
9
260.5796 397.8812 460.4757
488.9446 739.1081 884.9078
1198.3696 2627.3301 3761.6117

```

Appendix C6 Input file for HSS(=O)H

```

NAME (name of molecule)
hss(=o)h

COMMENTS:
b3_631gdp

TEMPERATURE
14 (Number of temperature to be read in)
 298 400 500 600 800 1000 1500 2000 2500 3000 3500 4000 4500 5000

ROTOR
1 number of internal rotors

MOLECULAR WT
 81.95471

OPTICAL ISOMER
1

MULTIPLICITY
1 multiplicity of molecular specie of interest

HF298
0

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 0 H 2 S 2 O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

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

rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
!1 (include decimal input)

MOMENT (1)=10 e-40 g*cm^2 (2)=GHZ (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3 choice of moment of inertia units
 87.93381 423.37242 493.34687

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)
9
260.5796 397.8812 460.4757
488.9446 739.1081 884.9078
1198.3696 2627.3301 3761.6117

```

Appendix C7 Input file for 'SSOH

NAME (name of molecule)

ssohR

COMMENTS:

b3_631gdp

TEMPERATURE

14 (Number of temperature to be read in)

298 400 500 600 800 1000 1500 2000 2500 3000 3500 4000 4500 5000

ROTOR

1 number of internal rotors

MOLECULAR WT

80.94688

OPTICAL ISOMER

1

MULTIPLICITY

2 multiplicity of molecular specie of interest

HF298

0

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

C 0 H 1 S 2 O 1

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

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

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

!1 (integer input)

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

!1 (include decimal input)

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

3 choice of moment of inertia units

73.90734 386.61948 457.28657

SYMMETRY

1

NON-LINEAR

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

6

113.7685

289.1405

619.1974

716.8910

1138.7324

3740.5306

Appendix C9 Input file for CH₃SSOCH₃

```

NAME (name of molecule)
ch3ssoch3

COMMENTS:
b3_631gdp

TEMPERATURE
15 (Number of temperature to be read in)
298 300 400 500 600 800 1000 1500 2000 2500 3000 3500 4000 4500 5000

ROTOR
2 number of internal rotors

MOLECULAR WT
109.98601

OPTICAL ISOMER
1

MULTIPLICITY
1 multiplicity of molecular specie of interest

HF298
0

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2 H 6 S 2 O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted. Will write to *.lst file as is).

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

rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
!1 (include decimal input)

MOMENT (1)=10 e-40 g*cm^2 (2)=GHZ (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3 choice of moment of inertia units
301.07941 1024.63242 1059.36895

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)
27
79.6357 117.7048 128.6639
173.6857 216.3571 307.3042
390.0600 488.1642 672.5043
680.4462 978.2428 982.0490
1024.1045 1172.7697 1191.7839
1360.5481 1471.1768 1474.9933
1491.3395 1493.4850 1513.5470
3028.4126 3065.1286 3103.0219
3135.0324 3159.0975 3177.2721

```

Appendix C8 Input file for $\text{CH}_2\text{SSO CH}_3$

```

NAME (name of molecule)
ch2ssoch3R

COMMENTS:
b3_631gdp

TEMPERATURE
15 (Number of temperature to be read in)
298 300 400 500 600 800 1000 1500 2000 2500 3000 3500 4000 4500 5000

ROTOR
2 number of internal rotors

MOLECULAR WT
108.97818

OPTICAL ISOMER
1

MULTIPLICITY
2 multiplicity of molecular specie of interest

HF298
0

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

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

rem USCALING FACTOR (User define scaling factors: ZPE, Hvib, Svib,
Cpvib)
!1 (include decimal input)

MOMENT (1)=10 e-40 g*cm^2 (2)=GHZ (3)=amu-Bohr^2 (4)=amu-Angstrom^2
3 choice of moment of inertia units
279.50475 1002.33060 1050.05231

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important. Units are cm-1)
24
72.0287 110.7656 161.1584
184.4265 234.8998 301.4647
381.4264 395.9647 438.5836
681.6228 787.8439 932.9218
1022.3041 1171.4344 1191.6399
1411.8400 1470.7677 1493.5175
1511.3972 3030.7401 3106.5201
3138.8946 3170.4748 3304.1719

```

APPENDIX D

INPUT FILES FOR INTERNAL ROTOR CONTRIBUTIONS CALCULATED BY ROTATOR PROGRAM

Input files to the program ROTATOR for the species presented in this thesis

Appendix D1 Input file for C-S rotor in CH₃SSOH

```
ir2-ch3ssoh,
8
```

1	6	0.000000	0.000000	0.000000
2	16	0.000000	0.000000	1.838330
3	1	1.021228	0.000000	-0.383030
4	1	-0.508696	-0.917731	-0.307335
5	1	-0.548965	0.864288	-0.374868
6	16	1.016469	1.717651	2.331472
7	8	-0.105164	2.986051	2.224826
8	1	-0.570658	3.017061	3.075826

```
1 2
1 3
3 4 5
2 3
6 7 8
```

$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx)$ b3lyp/6-31G(d,p)

```
0 0 1
```

```
1
```

```
300
```

```
5
```

```
0.5740
```

```
0.0100
```

```
-0.0346
```

```
0.5484
```

```
0.0284
```

```
-0.0202
```

```
-6.9454e-3
```

```
0.0757
```

```
0.0403
```

```
0.0877
```

```
-2.6755e-3
```

```
8
```

```
298. 500.
```

```
1200. 1500. 2000.
```

```
3000. 4000. 5000.
```


Appendix D2 Input file for C-S rotor in CH₃SS=O

```
ir1-ch3ssoR,
7
```

1	6	0.000000	0.000000	0.000000
2	16	0.000000	0.000000	1.830454
3	1	1.020883	0.000000	-0.384407
4	1	-0.527416	-0.899226	-0.320962
5	1	-0.538627	0.884769	-0.349652
6	16	-0.066573	2.124490	2.172524
7	8	-0.668542	2.807590	0.958915

```
1 2
1 3
3 4 5
2 2
6 7
```

$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx)$ b3lyp/6-31G(d,p)

```
0 0 1
```

```
1
```

```
300
```

```
5
```

```
0.1212
```

```
-2.6530e-4 -0.0183
```

```
0.0113 -6.7677e-3
```

```
-0.1668 -2.4959e-3
```

```
-0.0109 5.0150e-3
```

```
9.3293e-4 -3.6172e-3
```

```
8
```

```
298. 500.
```

```
1200. 1500. 2000.
```

```
3000. 4000. 5000.
```

Appendix D3 Input file for S-S rotor in CH₃SS=O

```
ir2-ch3ssoR,
7
```

1	6	0.000000	0.000000	0.000000
2	16	0.000000	0.000000	1.830655
3	1	1.035965	0.000000	-0.349339
4	1	-0.531750	-0.871538	-0.384183
5	1	-0.493091	0.918341	-0.321405
6	16	1.859101	-1.028936	2.173626
7	8	2.759955	-0.849559	0.966082

```
5 2
5 1
7
2 4
1 3 4 5
```

$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx)$ b31yp/6 -31G(d,p)

```
0 0 1
```

```
1
```

```
300
```

```
5
```

```
1.4421
```

```
-1.4622 8.1698e-4
```

```
-0.1484 -4.4156e-4
```

```
0.1195 -2.1822e-3
```

```
0.0689 -4.9195e-3
```

```
0.0445 -2.0914e-3
```

```
8
```

```
298. 500.
```

```
1200. 1500. 2000.
```

```
3000. 4000. 5000.
```

Appendix D4 Input file for C-S rotor in CH_2SSOH

ir3-ch2ssohR,

7

1	6	0.000000	0.000000	0.000000
2	16	0.000000	0.000000	1.727891
3	1	0.928753	0.000000	-0.556813
4	1	-0.960355	0.010657	-0.501295
5	16	1.746443	0.997322	2.288431
6	8	1.430669	2.655766	2.161474
7	1	1.019902	2.926567	2.998353

2 1

2 3

5 6 7

1 2

3 4

$$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx) \quad \text{b3l1yp/6-31G(d,p)}$$

0 0 1

1

300

5

0.7447

0.0265

0.0148

-0.9031

-1.2600e-3

-0.0312

0.0111

0.5953

-0.0736

7.4927e-3

-0.0233

11

298. 500.

1200. 1500. 2000. 2500.

3000. 3500. 4000. 4500. 5000.

Appendix D5 Input file for C-S rotor in CH₃SS(=O)H

ir1-ch3ss(=o)h,
8

1	6	-1.074665	-0.530778	-1.441878
2	16	-1.060507	-0.548772	0.388420
3	1	-0.036938	-0.537290	-1.790236
4	1	-1.566695	-1.447226	-1.771518
5	1	-1.606279	0.340901	-1.828391
6	16	0.762347	0.621700	0.662039
7	8	1.784969	0.235719	-0.370436
8	1	0.148709	1.775695	0.197548

1 2
1 3
3 4 5
2 3
6 7 8

$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx)$ b3lyp/6-31G(d,p)

0 0 1

1

300

5

0.9010

0.0208 -0.0224

0.0279 -7.3164e-3

0.1599 -0.9447

0.0155 -5.4215e-3

0.0187 0.0240

7

298. 1000.

1100. 1200.

2000. 3000. 5000.

Appendix D6 Input file for S-O rotor in SSOH

```
ir1-ssohR,
```

```
4
```

1	16	-0.359636	0.016941	-1.308875
2	16	-0.359709	0.018286	0.646419
3	8	1.224228	0.016599	1.226978
4	1	1.715688	-0.696431	0.783462

```
3 2
```

```
3 1
```

```
4
```

```
2 1
```

```
1
```

```
V(x) = A + B * COS(nx) + C * SIN(nx) b3lyp/6-31G(d,p)
```

```
0 0 1
```

```
1
```

```
300
```

```
5
```

```
0.8122
```

```
-1.1443 4.6909e-5
```

```
0.4401 -8.5452e-4
```

```
0.0192 1.7297e-4
```

```
-0.0189 -8.5177e-5
```

```
5.9529e-3 -2.6096e-4
```

```
8
```

```
298. 500.
```

```
1200. 1500. 2000.
```

```
3000. 4000. 5000.
```

Appendix D7 Input file for S-S rotor in HSS'=O

```
ir1-hssOR,
4
```

1	16	0	-1.303322	-0.372274	0.306457
2	1	0	-1.233195	0.351112	1.446250
3	16	0	0.523705	0.372143	-0.544771
4	8	0	1.713384	-0.043628	0.295845

```
1 3
1 1
2
3 1
4
```

$V(x) = A + B \cdot \cos(nx) + C \cdot \sin(nx)$ b31yp/6-31G(d,p)

```
0 0 1
```

```
1
```

```
300
```

```
5
```

```
0.7811
```

```
-0.6056                    1.1455e-3
```

```
0.5245                    -2.6605e-4
```

```
0.2071                    1.1607e-4
```

```
0.0312                    -5.8052e-4
```

```
0.0182                    3.0662e-4
```

```
7
```

```
2000. 2500
```

```
3000. 3500
```

```
4000. 4500. 5000.
```

Appendix D8 Input file for C-S rotor in CH₃SSOCH₃

```
ir1-ch3ssoch3,
11
```

1	6	0.209402	-1.453444	-1.903967
2	16	-0.421660	-1.309025	-0.182711
3	1	1.262092	-1.738978	-1.902778
4	1	-0.383946	-2.235609	-2.385201
5	1	0.070685	-0.511187	-2.434780
6	16	0.790691	0.127566	0.661873
7	8	0.170923	1.625426	0.182145
8	6	-0.956980	2.078528	0.942631
9	1	-0.728948	2.118233	2.013543
10	1	-1.178603	3.083635	0.574737
11	1	-1.827689	1.433330	0.778742

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

V(x)=A+B*COS(nx)+C*SIN(nx) b3lyp/6-31G(d,p)

```
0 0 1
```

```
1
```

```
300
```

```
5
```

```
0.5385
```

```
0.0136 -1.5195e-3
```

```
9.4083e-3 -4.1907e-3
```

```
0.5410 -0.0745
```

```
-0.0116 -2.5840e-3
```

```
-0.0118 2.2126e-4
```

```
8
```

```
298. 500.
```

```
1200. 1500. 2000.
```

```
3000. 4000. 5000.
```

Appendix D9 Input file for C-O rotor in CH₃SSOCH₃

```
ir3-ch3ssoch3,
11
```

1	6	0.209402	-1.453444	-1.903967
2	16	-0.421660	-1.309025	-0.182711
3	1	1.262092	-1.738978	-1.902778
4	1	-0.383946	-2.235609	-2.385201
5	1	0.070685	-0.511187	-2.434780
6	16	0.790691	0.127566	0.661873
7	8	0.170923	1.625426	0.182145
8	6	-0.956980	2.078528	0.942631
9	1	-0.728948	2.118233	2.013543
10	1	-1.178603	3.083635	0.574737
11	1	-1.827689	1.433330	0.778742

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

V(x)=A+B*COS(nx)+C*SIN(nx) b3lyp/6-31G(d,p)

```
0 0 1
1
300
5
0.8599
8.8397e-3 -2.8943e-3
0.0235 -0.0105
0.8130 -0.2503
-0.0237 5.9197e-3
-9.2276e-3 1.6039e-3
```

```
7
298. 1000.
1100. 1200.
2000. 3000. 5000.
```


Appendix D10 Input file for C-S rotor in $\text{CH}_2\text{SSOCH}_3$

```
ir1-ch2ssoch3,
10
```

1	6	0.876402	1.128235	-1.926119
2	16	0.866841	1.129990	-0.198098
3	1	1.836991	1.063502	-2.423014
4	1	-0.047870	1.179080	-2.488107
5	16	-0.941058	0.224030	0.348047
6	8	-0.729282	-1.440990	0.196134
7	6	-0.059162	-2.068099	1.299493
8	1	-0.565585	-1.857953	2.247696
9	1	-0.090179	-3.140654	1.092500
10	1	0.984928	-1.741184	1.362431

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

$V(x)=A+B*\text{COS}(nx)+C*\text{SIN}(nx)$ b3lyp/6-31G(d,p)

```
0 0 1
```

```
1
```

```
300
```

```
5
```

```
0.6432
```

```
-0.0684 0.1407
```

```
-0.3282 -0.6216
```

```
0.1448 -0.0137
```

```
-0.1527 0.3971
```

```
-0.0555 -0.1084
```

```
10
```

```
298. 500. 1000.
```

```
2000. 2500. 3000.
```

```
3500. 400. 4500. 5000.
```

Appendix D11 Input file for C-O rotor in $\text{CH}_2\text{SSOCH}_3$

```
ir4-ch3ssoch3,
10
```

1	6	0.876402	1.128235	-1.926119
2	16	0.866841	1.129990	-0.198098
3	1	1.836991	1.063502	-2.423014
4	1	-0.047870	1.179080	-2.488107
5	16	-0.941058	0.224030	0.348047
6	8	-0.729282	-1.440990	0.196134
7	6	-0.059162	-2.068099	1.299493
8	1	-0.565585	-1.857953	2.247696
9	1	-0.090179	-3.140654	1.092500
10	1	0.984928	-1.741184	1.362431

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

$V(x)=A+B*\text{COS}(nx)+C*\text{SIN}(nx)$ b3lyp/6-31G(d,p)

```
0 0 1
```

```
1
```

```
300
```

```
5
```

```
0.8728
```

```
-0.0892 0.1389
```

```
-0.0966 -0.1439
```

```
0.4343 0.6430
```

```
0.0824 0.0994
```

```
-0.0485 0.0561
```

```
10
```

```
298. 500. 1000.
```

```
2000. 2500. 3000.
```

```
3500. 400. 4500. 5000.
```

APPENDIX E

OPTIMIZED Z-MATRIX FROM B3LYP/6-31G (d, p)

Optimized Z-matrix for the species presented in this thesis

**Appendix E1 Optimized Z-matrix from B3LYP/6-31G (d, p) for CH₃SSOH,
CH₃SS(=O)H, CH₃SS[·]=O and [·]CH₂SSOH**

CH ₃ SSOH	CH ₃ SS (=O) H	CH ₃ SS [·] =O	[·] CH ₂ SSOH
C	C	C	C
S, 1, r21	S, 1, B1	S, 1, r21	S, 1, r21
H, 1, r31, 2, a312	H, 1, B2, 2, A1	H, 1, r31, 2, a312	H, 1, r31, 2, a312
H, 1, r41, 2, a412, 3, d4123, 0	H, 1, B3, 2, A2, 3, D1, 0	H, 1, r41, 2, a412, 3, d4123, 0	H, 1, r41, 2, a412, 3, d4123, 0
H, 1, r51, 2, a512, 3, d5123, 0	H, 1, B4, 2, A3, 4, D2, 0	H, 1, r51, 2, a512, 3, d5123, 0	S, 2, r52, 1, a521, 3, d5213, 0
S, 2, r62, 1, a621, 3, d6213, 0	S, 2, B5, 1, A4, 4, D3, 0	S, 2, r62, 1, a621, 3, d6213, 0	O, 5, r65, 2, a652, 1, d6521, 0
O, 6, r76, 2, a762, 1, d7621, 0	O, 6, B6, 2, A5, 1, D4, 0	O, 6, r76, 2, a762, 1, d7621, 0	H, 6, r76, 5, a765, 1, d7651, 0
H, 7, r87, 6, a876, 2, d8762, 0	H, 6, B7, 2, A6, 1, D5, 0	Variables:	Variables:
Variables:	Variables:	r21=1.83078171	r21=1.7278414
r21=1.8383301	B1=1.83044132	r31=1.09084113	r31=1.08287113
r31=1.0906966	B2=1.09465741	r41=1.09075295	r41=1.0833634
r41=1.09336966	B3=1.09116124	r51=1.09311219	r52=2.08774626
r51=1.0903591	B4=1.09171001	r62=2.15321433	r65=1.69295234
r62=2.05589967	B5=2.18349949	r76=1.51683246	r76=0.97078554
r76=1.69654726	B6=1.50357617	a312=110.67512011	a312=120.93898566
r87=0.97048773	B7=1.387087	a412=107.04971634	a412=117.55819478
a312=110.55946989	A1=108.10860497	a512=108.66665978	a521=105.60482961
a412=106.32526784	A2=107.29600786	a621=99.13115752	a652=106.97590872
a512=110.10870109	A3=111.44646049	a762=109.23119195	a765=106.71281175
a621=103.87868449	A4=97.26680918	d4123=120.33493489	d4123=-179.24478202
a762=106.4202714	A5=110.12882626	d5123=-121.44306616	d5213=29.72892473
a876=106.61129892	A6=91.9877312	d6213=91.79484477	d6521=80.45428996
d4123=118.99948802	D1=117.47958913	d7621=24.46236303	d7651=118.45973994
d5123=-122.42227841	D2=120.6304162		
d6213=59.38385256	D3=150.82002628		
d7621=81.93370196	D4=-39.1412079		
d8762=84.948916	D5=69.27499323		

**Appendix E2 Optimized Z-matrix from B3LYP/6-31G (d, p) for HSSOH,
HSS(=O)H, HSS=O and SSOH**

HSSOH	HSS (=O)H	HSS =O	SSOH
S	S	S	S
H,1,r21	H,1,B1	H,1,r21	S,1,r21
S,1,r31,2,a312	S,1,B2,2,A1	S,1,r31,2,a312	O,2,r32,1,a321
O,3,r43,1,a431,2,d4312,0	H,3,B3,1,A2,2,D1,0	O,3,r43,2,a432,1,d4321,0	H,3,r43,2,a432,1,d4321,0
H,4,r54,3,a543,1,d5431,0	O,3,B4,1,A3,2,D2,0	Variables:	Variables:
Variables:	Variables:	r21=1.35178851	r21=1.95529458
r21=1.3550719	B1=1.34977143	r31=2.14866759	r32=1.6869813
r31=2.0747551	B2=2.19967835	r43=1.51487236	r43=0.9729604
r43=1.68787042	B3=1.38791536	a312=95.99982656	a321=110.12714298
r54=0.9707062	B4=1.49277934	a432=95.81726132	a432=108.54945343
a312=99.8904746	A1=93.70459039	d4321=-121.80423762	d4321=-50.53127601
a431=106.15843093	A2=85.33722116		
a543=106.89533992	A3=114.04808667		
d4312=-84.0067879	D1=-164.28121575		
d5431=-85.50705504	D2=87.25604374		

Appendix E3 Optimized Z-matrix from B3LYP/6-31G (d, p) for CH₃SSOCH₃, and ·CH₂SSOCH₃

CH₃SSOCH₃

C
 S,1,r21
 H,1,r31,2,a312
 H,1,r41,2,a412,3,d4123,0
 H,1,r51,2,a512,3,d5123,0
 S,2,r62,1,a621,3,d6213,0
 O,6,r76,2,a762,1,d7621,0
 C,7,r87,6,a876,2,d8762,0
 H,8,r98,7,a987,6,d9876,0

 H,8,r108,7,a1087,9,d10879,0

 H,8,r118,7,a1187,10,d118710,0

 Variables:
 r21=1.83897105
 r31=1.09072811
 r41=1.09335654
 r51=1.09034582
 r62=2.06080372
 r76=1.69051346
 r87=1.43380858
 r98=1.09564018
 r108=1.09302485
 r118=1.09602587
 a312=110.53205938
 a412=106.37497653
 a512=110.12949396
 a621=103.67806846
 a762=106.59966892
 a876=114.70098195
 a987=111.47863287
 a1087=105.75789719
 a1187=111.07528011
 d4123=119.01798616
 d5123=-122.33115009
 d6213=58.99815532
 d7621=81.49107467
 d8762=80.44689271
 d9876=55.85046488
 d10879=119.22800082
 d118710=118.43188017

·CH₂SSOCH₃

C
 S,1,r21
 H,1,r31,2,a312
 H,1,r41,2,a412,3,d4123,0
 S,2,r52,1,a521,3,d5213,0
 O,5,r65,2,a652,1,d6521,0
 C,6,r76,5,a765,2,d7652,0
 H,7,r87,6,a876,5,d8765,0
 H,7,r97,6,a976,5,d9765,0

 H,7,r107,6,a1076,5,d10765,0

Variables:

r21=1.72804774
 r31=1.08343336
 r41=1.0829097
 r52=2.09464516
 r65=1.68529392
 r76=1.43517514
 r87=1.0953148
 r97=1.09278651
 r107=1.09588254
 a312=117.61893671
 a412=120.94291261
 a521=105.3708621
 a652=107.17836951
 a765=114.90244465
 a876=111.45814609
 a976=105.66366857
 a1076=111.01804293
 d4123=179.33699173
 d5213=-149.49492973
 d6521=79.35793814
 d7652=80.84144456
 d8765=55.36918582
 d9765=174.62390166
 d10765=-66.97230467

APPENDIX F

LIST OF ENERGIES CALCULATED USING B3LYP/6-31G (d, p), B3LYP/6-311++G (3df, 2p) AND CBS-QB3

List of energies for the parent and reference species presented in this thesis

Appendix F1 List of Energies for the Parent Species

Species	Energy in Hartrees		
	B3LYP/6-31G (d, p)	B3LYP/6-311++G (3df, 2p)	CBS-QB3
CH ₃ SSOH	-912.0404383	-912.162441	-911.03635
CH ₃ SS(=O)H	-912.0022002	-912.1361146	-911.01168
CH ₃ SS'=O	-911.4252196	-911.5505085	-910.425023
·CH ₂ SSOH	-911.3877641	-911.5131084	-910.383028
HSSOH	-872.7510126	-872.8633697	-871.810461
HSS(=O)H	-872.7144868	-872.8404051	-871.788268
HSS'=O	-872.1359678	-872.2525627	-871.200048
·SSOH	-872.1479125	-872.2608154	-871.207396
CH ₃ SSOCH ₃	-951.3179301	-951.4476475	-950.247667
·CH ₂ SSOCH ₃	-950.6644836	-950.7973246	-949.594152

Appendix F2 List of Energies for the Reference Species

Species	Energy in Hartrees		
	B3LYP/6-31G (d, p)	B3LYP/6-311++G (3df, 2p)	CBS-QB3
C ₂ H ₆	-79.76083556	-79.78359386	-79.626119
CH ₄	-40.476056	-40.4887964	-40.406185
HSH	-399.3730069	-399.4103369	-398.931111
CH ₃ SH	-438.6557805	-438.7025704	-438.148253
CH ₃ OH	-115.6693117	-115.7182667	-115.535673
CH ₃ SSH	-836.8364619	-836.9194279	-835.902689
CH ₃ SCH ₃	-477.9419497	-477.9982167	-477.370613
CH ₃ SOH	-513.8381582	-513.9237902	-513.269424
C ₂ H ₅ OH	-154.9676045	-155.0263811	-154.76488
HSSH	-797.5482012	-797.6219347	-796.67016
CH ₃ S(=O)H	-513.8105466	-513.9098372	-513.256135
C ₂ H ₅ SH	-477.943607	-478.000682	-477.373385
HSOH	-474.5451671	-474.6209277	-474.040578
CH ₃ SSCH ₃	-876.1240896	-876.2172421	-875.118794
CH ₃ SC ₂ H ₅	-517.2295132	-517.2963094	-516.595738
CH ₃ O [·]	-115.0147854	-115.059384	-114.870514
C ₂ H ₅ O [·]	-154.309699	-154.3638915	-154.100554
CH ₃ S [·] =O	-513.2329902	-513.3224486	-512.667759
CH ₃ S [·]	-438.0249479	-438.0686994	-437.512066
[·] CH ₂ SH	-438.0044424	-438.0551627	-437.498456
CH ₃ C [·] HSH	-477.2968692	-477.3568315	-476.725965
HS [·] =O	-473.9336888	-474.0023138	-473.432549
[·] SH	-398.7340004	-398.7340004	-398.287356
[·] CH ₂ SCH ₃	-477.2925245	-477.3532173	-476.722804

REFERENCES

1. Bates T. S, Lamb B. K, A.Guenther, Dignon J, Stoiber R. E, Sulfur Emissions to the Atmosphere from Natural Sources, *Journal of Atmospheric Chemistry*, 14, 315-337, 1992.
2. Masahiro Utiyama, Tsutoma Fukuyama, Kazuhiko Sakamoto, Hidekazu Ishihara, Atsuyuki Sorimachi, Takeshi Tanonaka, Xuhui Dong, Hao Quan, Wei Wang and Dagang Tang, *Atmospheric Environment*, Vol 39, Issue 2, January 2005, pp 329-335.
3. Li Zhu and J. W. Bozzelli, The Multi-Channel Reaction of $\text{CH}_3\text{S}+\text{O}_2$: Thermochemistry and kinetic barriers, *Journal of Molecular Structure: Thermochem* 728 (2005) 147-157.
4. *Environmental Health Perspectives* Volume 102, Number 2, February 1994.
5. Xiaoyan Li, Hongmin Fan, Lingpeng Meng, Yanli Zeng, Shijun Zheng, Theoretical Investigation on Stability and Isomerizations of CH_3SO Isomers., Dec 2007, 111(12) 2343- 2350.
6. Rubik Asatryan. Joseph W. Bozzelli, John M.Simmie, Thermochemistry for Enthalpies and Reaction Paths of Nitrous Acid Isomers, *International Journal of Chemical Kinetics* 39: 378-398, 2007.
7. Li Zhu and J.W Bozzelli, Reaction Paths, Kinetics and Thermochemical Properties of Thioformyl Radical with O_2 Reaction, 5th US combustion meeting, 2007.
8. Sheng C, Ph.D. Dissertation. Department of Chemical Engineering, New Jersey Institute of Technology, Newark, NJ, 2002.
9. T.H Lay, Krasnoperov , L.N, Venanzi, C.A, Bozzelli, J.W.J.Phys, Chem.1996, 100, 8240.
10. Shokhirev N.V, University of Arizona, Tempe, Arizona, <http://www.chem.arizona.edu/faculty/walk/nikolai/programs.html#programs>.
11. Cox J.D , D.D.Wagman, V.A. Medvedev, CODATA key values for Thermodynamics, Hemisphere Publishing Corp., New York, 1984.
12. Hynes A. J, Wine P. H, Kinetics and Mechanisms of the Oxidation of Gaseous Sulfur Compounds, in: *Gas-Phase Combustion Chemistry*, ed. W.C. Gardiner, Jr., 1999, Springer-Verlag, NY, 1999, pp. 343-388.
13. F. Jin , J.W.Bozzelli , 2004, CBS-QB3 method , M.S. Thesis in Chemistry, New Jersey Institute of Technology, Newark, NJ, 2003.

14. Turecek. F, J. Phys. Chem., 1994, 98, 3701.
15. Florent Domine, Timothy P.Murrells, and Carleton J. Howard , Hanes, Kinetics of the Reactions of NO₂ with CH₃S, CH₃SO,CH₃SS and CH₃SSO at 297K and 1 Torr , J.T.J. Phys.Chem. 1990, 94, 2736.
16. Chase M.W, Jr., NIST-JANAF Thermochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph 9, 1998, 1-1951.
17. Pittam D.A, Pilcher. G, Measurements of Heats of Combustion by Flame Calorimetry. Part 8.-Methane, ethane, propane, n-butane and 2-methylpropane, J. Chem. Soc. Faraday Trans. 1, 1972, 68, 2224-2229.
18. Tsang W, Heats of Formation of Organic Free Radicals by Kinetic Methods in Energetics of Organic Free Radicals, Martinho Simoes, J.A, Greenberg, A, Liebman, J.F., eds., Blackie Academic and Professional, London, 1996, 22-58.
19. Green J.H.S, Revision of the values of the heats of formation of normal alcohols, Chem. Ind. (London), 1960, 1215-1216.
20. Good W.D, Lacina. J.L, McCullough J.P, Methanethiol and Carbon disulfide: Heats of Combustion and Formation by Rotating-bomb Calorimetry, J. Phys. Chem., 1961, 65, 2229-2231.
21. Liming Wang, Jingsong Zhang, Ab initio Calculations on Thermochemistry of CH₃SO_xH (x=1-3) and H₂SO_y (y=2,3), Journal of Molecular Structure (Theochem) 581 (2002) 129-138.
22. Chase M.W, Jr., NIST-JANAF Thermochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph 9, 1998, 1-1951.
23. (a) Schurath, U, Weber, M Becker, K.H.J. Chem. Phys. 1977,67,110.(b) Iraqi, M, Goldberg N, Schwarz H.J. Phys. Chem. 1994, 98,2015. (c) Bowie J.H, Stringer M. B, Haynes R. N. Rapid Commun. Mass Spectrom. 1990, 4, 129. (d) O’Hair, R.A.J, Depuy, C.H.Bierbaum, V.M.J. Phys. Chem. 1993,75,7955.
24. Giulia de Petris, Marzio Rosi, and Anna Troiani, SSOH and HSSO Radicals: An Experimental and Theoretical Study of [S₂OH]^{0/+/-} species, J. Phys. Chem. A 2007, 111, 6526-6533.
25. (a) Decker B.K, Adams N.G. Int. J. Mass Spectrum. Ion Process. 1997, 165/166, 257. (b) Decker B.K, Adams N.G, Babcock L.M. Int. J. Mass Spectrom. 1999, 185/186/187, 727.
26. (a) Block E, O’Connor, J.J Am.Chem. Soc. 1974, 96, 3921. (b) Schmidth H, Steudel R, Sulzle D, Schwarz H, Inorg.Chem. 1992, 31, 941.
27. Justin Jee and Fu-Ming Tao, J. Phys. Chem., 2006, 110, 7682 – 7689.