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Structure and thermochemistry of disulfide-oxygen species

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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 $Cp(T)$) on the S-S bridge system in the sulfur bridged molecules CH_3SSOH, $CH_3SS(=O)H$, HSSOH, HSS(=O)H and CH_3SSOCH_3 and the their radicals corresponding to H atom loss. Structure and thermochemical parameters (S° and $Cp(T)$) 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, $CH_3SS(=O)H$, $CH_3SS^\bullet{=}O$ and $^\bullet CH_2SSOH$ 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 CH_3SSO—H hydrogen atom to form the more stable $CH_3SS^\bullet{=}O$ structure. The C—H bond energy of $CH_3SS(=O)H$ is remarkably weak at only 77.01 kcal mol^{-1} and results in the formation of $^\bullet CH_2SSOH$ radical by the loss of H— $CH_2SS(=O)H$ 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 $CH_3SS(=O)$—H hydrogen atom forms a $CH_3SS^{\bullet}=O$ radical.

Enthalpies of formation for HSSOH, HSS(=O)H, $HSS^{\bullet}=O$ 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 $^{\bullet}$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 $HSS^{\bullet}=O$ radical.

Enthalpies of formation for CH_3SSOCH_3 and the radical $^{\bullet}CH_2SSOCH_3$ are -34.33 kcal mol-1 and 11.4 kcal mol-1 respectively. It is important to note that as the CH_3SSOC•H2 radical is formed it immediately dissociates to lower energy products CH3SS$^{\bullet}$(=O) + $CH_2=O$ with no significant LT 6 kcal mol-1) barriers. This $CH_3SSOC^{\bullet}H_2$ radical does not exist.

STRUCTURE AND THERMOCHEMISTRY OF DISULFIDE-OXYGEN SPECIES

by
Shyamala Pravin Pillai

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STRUCTURE AND THERMOCHEMISTRY OF DISULFIDE-OXYGEN SPECIES

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To my beloved son, Mayaank.

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LIST OF SYMBOLS

$\Delta Hrxn$	Heat of Reaction
ΔH^{o}_{f}	Heat of Formation
I	Moments of Inertia
$S^{\circ}298$	Entropy at 298 K
$Cp^{\circ}(T)$	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^o, S^o and Cp(T)) on the S-S-O bridge systems. Structure and thermochemical parameters (S^o and Cp(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 are isodesmic in most cases. Contributions to S^o298 and $Cp^o(T)$ 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 $CH_3SS(=O)H$ and the two radicals corresponding to H atom loss $CH_3SS^•{=}O$ and $^•CH_2SSOH$. Chapter 3 will deal with HSSOH and HSS(=O)H and the two radicals corresponding to H atom loss $HSS^•{=}O$ and $^•SSOH$. The two aforementioned radicals, $CH_3SS^•{=}O$ and $^•CH_2SSOH$, can originate from either or both the parent molecules viz: CH_3SSOH and $CH_3SS(=O)H$. Similarly the radicals $HSS^•{=}O$ and $^•SSOH$ can originate from either or both the parent molecules viz: HSSOH and HSS(=O)H. Chapter 4 talks on the CH_3SSOCH_3 and its radicals $•CH_2SSOCH_3$ and $CH_3SSOC•H_2$.

CHAPTER 2

STRUCTURAL AND THERMOCHEMICAL STUDIES ON S-S-O BRIDGED SYSTEM IN CH_3SSOH AND $CH_3SS(=O)H$ 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 ($CH_3S\bullet$) with $^3O_2$ 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 $CH_3S + O_2 \leftrightarrow CH_3S$-OO reaction has a very shallow well, ~ 10 kcal mol^{-1}, which results in very rapid reverse reaction to back to CH_3S• and a quasi equilibrium. The CH_3S and CH_3SOO can react with hydroperoxides (e.g. HO_2, CH_3SOO.) or OH or NOx to form the CH_3SO moiety, which exists as CH_3S•(=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]. CH_3S•=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 CH_3S•=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 CH_3SS•=O radical can be formed by the reaction $CH_3SS + NO_2 \rightarrow CH_3SS$•=O + NO and CH_3SS•=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 CH_3SSOH 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 Cp° (T) of each species are calculated using the "SMCPS" (Statistical Mechanics for Heat Capacity and Entropy Cp 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 Cp° (T).

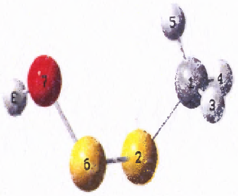
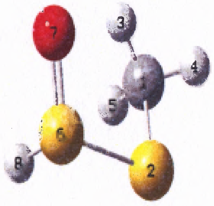
2.3 Results and Discussion

2.3.1 Structure

The S—O bond in CH_3SSOH is 1.69A°, while S—O bond distance in CH3SS·=O exhibits shorter bond length of 1.51A°. The C—S bond in CH_3SSOH is 1.83A° against the 1.72A° in ·CH2SSOH. In $CH_3SS(=O)H$, the S—O bond is 1.5A° and the C—S bond is 1.83A°. The shorter bond distance of 1.51A° in S-O bond in $CH_3SS^{\cdot}=O$ predicts the presence of double bond.

The formation of $CH_3SS{\cdot}=O$ is accompanied by reduction of the S-S-C bond angle to 99.13°,while formation of $C{\bullet}H_2SSOH$ reveals increase in bond angle S-S-C to 105.6 ° compared to the S-S-C bond angle of 103.87 ° in CH_3SSOH as listed in Table 2.1.

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

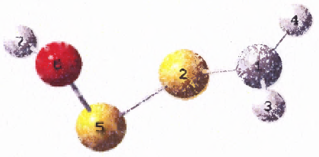
CH$_3$SSOH	**CH$_3$SS(=O)H**
	

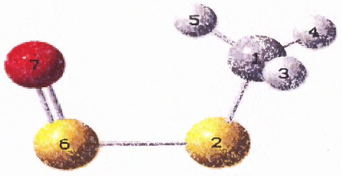
	CH$_3$SSOH			CH$_3$SS(=O)H	
R1	R(1,2)	1.838	R1	R(1,2)	1.830
R2	R(1,3)	1.090	R2	R(1,3)	1.094
R3	R(1,4)	1.093	R3	R(1,4)	1.091
R4	R(1,5)	1.090	R4	R(1,5)	1.091
R5	R(2,6)	2.055	R5	R(2,6)	2.183
R6	R(6,7)	1.696	R6	R(6,7)	1.503
R7	R(7,8)	0.970	R7	R(6,8)	1.387
A1	A(2,1,3)	110.55	A1	A(2,1,3)	108.10
A2	A(2,1,4)	106.32	A2	A(2,1,4)	107.29
A3	A(2,1,5)	110.10	A3	A(2,1,5)	111.44
A4	A(3,1,4)	109.68	A4	A(3,1,4)	109.04
A5	A(3,1,5)	110.52	A5	A(3,1,5)	110.71
A6	A(4,1,5)	109.53	A6	A(4,1,5)	110.12
A7	A(1,2,6)	103.87	A7	A(1,2,6)	97.26
A8	A(2,6,7)	106.420	A8	A(2,6,7)	110.12

Table 2.1 Continued

A9	A(6,7,8)	106.611
D1	D(3,1,2,6)	59.383
D2	D(4,1,2,6)	178.383
D3	D(5,1,2,6)	-63.038
D4	D(1,2,6,7)	81.933
D5	D(2,6,7,8)	84.948

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





$^{\bullet}\mathrm{CH_2SSOH}$

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

$\mathrm{CH_3SS^{\bullet}(=O)}$

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_3SSOH			
	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
$\cdot CH_2SSOH$			
	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
$CH_3SS^{\cdot}{=}O$			
	Figure 7	D(3,1,2,6)	91.7948
	Figure 8	D(1,2,6,7)	24.4624
CH3SS(=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 CH_3SSOH and $CH_3SS(=O)H$ and S=O bond in $CH_3SS^{\cdot}{=}O$ are all polar covalent bonds. In CH_3SSOH, 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 A°) is shorter than C—S (1.84 A°) bond in CH_3SSOH. The C—S bond in $\cdot CH_2SSOH$ is 1.72A° and is slightly shorter than theC—S bond in CH_3SSOH. 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 CH_3SSOH.

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

CH_3SSOH		$CH_3SS(=O)H$		$CH_3SS^{\bullet}{=}O$		$^{\bullet}CH_2SSOH$	
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 CH_3SSOH and $CH_3SS(=O)H$ molecule and their two radicals, CH3SS˙=O and ·CH2SSOH respectively. The enthalpy calculations are based on the lowest energy conformer.

Work reactions for CH_3SSOH:

$CH_3SSOH + C_2H_6 \rightarrow CH_3SSH + CH_3CH_2OH$ (1)

$CH_3SSOH + C_2H_6 \rightarrow CH_3SCH_3 + CH_3SOH$ (2)

$CH_3SSOH + CH_4 \rightarrow CH_3SH + CH_3SOH$ (3)

$CH_3SSOH + HSH \rightarrow CH_3SOH + HSSH$ (4)

$CH_3SSOH + CH_3SH \rightarrow CH_3SSH + CH_3SOH$ (5)

$CH_3SSOH + CH_3OH \rightarrow CH_3SOH + CH_3SOH$ (6)

Work reactions for $CH_3SS(=O)H$:

$CH_3SS(=O)H + C_2H_6 \rightarrow CH_3S(=O)H + CH_3SCH_3$ (7)

$CH_3SS(=O)H + CH_4 \rightarrow CH_3S(=O)H + CH_3SH$ (8)

$CH_3SS(=O)H + CH_3OH \rightarrow CH_3S(=O)H + CH_3SOH$ (9)

Work reactions for $CH_3SS^{\bullet}=O$:

$CH_3SS^{\bullet}=O + CH_3OH \rightarrow CH_3SSOH + CH_3O^{\bullet}$ (10)

$CH_3SS^{\bullet}=O + C_2H_5OH \rightarrow CH_3SSOH + C_2H_5O^{\bullet}$ (11)

$CH_3SS^{\bullet}=O + CH_3SOH \rightarrow CH_3SSOH + CH_3S=O^{\bullet}$ (12)

$CH_3SS^{\bullet}=O + CH_3S(=O)H \rightarrow CH3S^{\bullet}=O + CH_3SS(=O)H$ (13)

$CH_3SS^{\bullet}=O + CH_3SH \rightarrow CH_3S^{\bullet} + CH_3SS(=O)H$ (14)

Work reactions for $^{\bullet}CH_2SSOH$

$^{\bullet}CH_2SSOH + CH_3SH \rightarrow CH_3SSOH + {}^{\bullet}CH_2SH$ (15)

$^{\bullet}CH_2SSOH + C_2H_5SH \rightarrow CH_3SSOH + CH_3\ {}^{\bullet}CHSH$ (16)

$^{\bullet}CH_2SSOH + CH_3SH \rightarrow CH_3SSOH + {}^{\bullet}CH_2SH$ (17)

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 $\Delta H_{rxn(298)}$ (kcal mol^{-1}) from isodesmic reactions.

Isodesmic reaction	B3LYP/6-31G (d, p)	B3LYP/6-311++G (3df, 2p)	CBSQB3
Work reactions for CH_3SSOH:			
$CH_3SSOH + C_2H_6 \rightarrow CH_3SSH + CH_3CH_2OH$	-1.75	0.1417	-8.59
$CH_3SSOH + C_2H_6 \rightarrow CH_3SCH3 + CH_3SOH$	13.28	15.08	12.12
$CH_3SSOH + CH_4 \rightarrow CH_3SH + CH_3SOH$	14.15	15.61	11.68
$CH_33SSOH + HSH \rightarrow CH_3SOH + HSSH$	16.99	16.97	17.49
$CH_3SSOH + CH_3SH \rightarrow CH_3SSH + CH_3SOH$	13.55	13.67	7.837
$CH_3SSOH + CH_3OH \rightarrow CH_3SOH + CH_3SOH$	20.98	20.78	20.81
Work reactions for $CH_3SS(=O)H$:			
$CH_3SS(=O)H + C_2H_6 \rightarrow CH_3S(=O)H + CH_3SCH_3$	6.61	7.31	6.93
$CH_3SS(=O)H + CH_4 \rightarrow CH_3S(=O)H + CH_3SH$	7.49	7.85	8.45
$CH_3SS(=O)H + CH_3OH \rightarrow CH_3S(=O)H + CH_3SOH$	14.31	13.02	13.67
Work reactions for $CH_3SS\cdot{=}O$:			
$CH_3SS^{\cdot}{=}O + CH_3OH \rightarrow CH_3SSOH + CH_3O^{\cdot}$	24.66	29.46	33.78
$CH_3SS^{\cdot}{=}O + C_2H_5OH \rightarrow CH_3SSOH + C_2H_5O^{\cdot}$	26.79	31.73	33.25
$CH_3SS^{\cdot}{=}O + CH_33S(=O)H \rightarrow CH_3S^{\cdot}{=}O + CH_3SS(=O)H$	0.3612	-11.18	-1.078
$CH_3SS^{\cdot}{=}O + CH_3SH \rightarrow CH_3S^{\cdot} + CH_3SS(=O)H$	-33.79	-30.28	-31.08
$CH_3SS^{\cdot}{=}O + CH_3SOH \rightarrow CH_3SSOH + CH_3S^{\cdot}{=}O$	-6.30	-6.64	-6.06
Work reactions for $^{\cdot}CH_2SSOH$:			
$^{\cdot}CH_2SSOH + CH_3SH \rightarrow CH_3SSOH + {}^{\cdot}CH_2SH$	-0.8383	-1.20	-2.21
$^{\cdot}CH_2SSOH + C_2H_5S \rightarrow CH_3SSOH + CH_3\,{}^{\cdot}CHSH$	-3.73	-3.44	-3.703
$^{\cdot}CH_2SSOH + CH_3SCH_3 \rightarrow CH_3SSOH + {}^{\cdot}CH_2SCH_3$	-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
Enthalpies of Formation of CH_3SSOH:			
$CH_3SSOH + C_2H_6 \rightarrow CH_3SSH + CH_3CH_2OH$	-35.62	-37.46	-34.17
$CH_3SSOH + C_2H_6 \rightarrow CH_3SCH_3 + CH_3SOH$	-36.08	-37.88	-36.88
$CH_3SSOH + CH_4 \rightarrow CH_3SH + CH_3SOH$	-35.63	-37.09	-37.08
$CH_3SSOH + HSH \rightarrow CH_3SOH + HSSH$	-42.02	-41.99	-42.51
$CH_3SSOH + CH_3SH \rightarrow CH_3SSH + CH_{3}3SOH$	-43.22	-43.35	-37.51
$CH_3SSOH + CH_3OH \rightarrow CH_3SOH + CH_3SOH$	-41.74	-42.55	-42.58
Average	-39.05	-40.05	**- 38.46**
Mean of averages	***-39.19***		
Enthalpies of Formation of $CH_3SS(=O)H$:			
$CH_3SS(=O)H + C_2H_6 \rightarrow CH_3S(=O)H + CH_3SCH$	-16.11	-16.81	-16.43
$CH_3SS(=O)H + CH_4 \rightarrow CH_3S(=O)H + CH_3SH$	-15.67	-16.03	- 16.64
$CH_3SS(=O)H + CH_3OH \rightarrow CH_3S(=O)H + CH_3SOH$	-20.77	-19.48	-20.14
Average	**-17.52**	**-17.44**	**-17.74**
Mean of averages	***-17.57***		

Table 2.5 continued

Isodesmic reaction	B3LYP/6-31G(d,p)	B3LYP/6-311++G(3df,2p)	CBSQB3
Enthalpies of Formation of $CH_3SS^{\bullet}=O$:			
$CH_3SS^{\bullet}=O + CH_3OH \rightarrow CH_3SSOH + CH_3O^{\bullet}$	-11.97	-15.78	-20.10
$CH_3SS^{\bullet}=O + C_2H_5OH \rightarrow CH_3SSOH + C_2H_5O^{\bullet}$	-12.97	-17.92	-19.45
$CH_3SS^{\bullet}=O + CH_3S(=O)H \rightarrow CH_3S^{\bullet}=O + CH_3SS(=O)H$	-15.81	-16.57	-16.53
$CH_3SS^{\bullet}=O + CH_3SH \rightarrow CH_3S^{\bullet} + CH_3SS(=O)H$	-16.16	-12.66	-13.45
$CH_3SS^{\bullet}=O + CH_3SOH \rightarrow CH_3SSOH + CH_3S^{\bullet}=O$	-16.56	-16.22	-15.80
Average	- 14.92	- 15.83	- 17.02
Mean of averages	***-15.92***		
Enthalpies of Formation of $^{\bullet}CH_2SSOH$			
$^{\bullet}CH_2SSOH + CH_3SH \rightarrow CH_3SSOH + {}^{\bullet}CH_2SH$	5.55	5.92	6.92
$^{\bullet}CH_2SSOH + C_2H_5SH \rightarrow CH_3SSOH + CH_3{}^{\bullet}CHSH$	6.89	6.61	6.87
$^{\bullet}CH_2SSOH + CH_3SCH_3 \rightarrow CH_3SSOH + {}^{\bullet}CH_2SCH_3$	6.30	6.98	7.72
Average	6.25	6.50	7.17
Mean of averages	***6.64***		

Table 2.6 Enthalpies of formation (in kcal mol^{-1}) of reference species in work reactions

Species	ΔH^{o}_{f298}	Species	ΔH^{o}_{f298}
H [11]	52.1	C_2H_6 [17]	-20.04
CH_4 [16]	-17.89	CH_3SSH [20]	-1.24
CH_3SCH_3 [11]	-8.94	CH_3SH [20]	-5.47
C_2H_5OH [19]	-56.17	CH_3SOH [14]	-33.9
C_2H_5SH [12]	-10.99	CH_3OH [19]	-48.04
$\cdot CH_2SCH_3$ [12]	33.78	$CH_3\ \cdot CHSH$ [28]	30.64
$\cdot CH_2SH$ [3]	37.7	$CH_3SO\cdot$ [13]	18.31
$C_2H_5O\cdot$ [28]	-3.9	$CH_3O\cdot$.[18]	4.1
$CH_3S(=O)H$ [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 CH_3SSOH is calculated using [CH_3SSOH- [(H$^\cdot$ + $^\cdot CH_2SSOH$)]] reaction and the bond energy of O—H in CH_3SSOH is calculated using [CH_3SSOH- [(H$^\cdot$ + $CH_3SSO^\cdot$)]]. Similarly, the bond energy of C—H bond in

$CH_3SS(=O)H$ is calculated using [$CH_3SS(=O)H$- [($H^\bullet$ + $^\bullet CH_2SSOH$)]] reaction and the bond energy of S—H in CH_3SSOH is calculated using [$CH_3SS(=O)H$- [($H^\bullet$ + $CH_3SS^\bullet{=}O$)]] 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
CH_3SSOH:				
C-H bond	-97.4	-98.65	-97.73	-97.93
O-H bond	-76.23	-76.32	- 73.54	-75.36
$CH_3SS(=O)H$:				
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 fromTable 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 $CH_3SS(=O)H$ is 77.01 kcal mol^{-1}. And the bond energy of S—H in $CH_3SS(=O)H$ 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

	Moment of Inertia, units amu(Bohr)^2			frequencies (cm^{-})					
Species	*I 1*	*I 2*	*I 3*	*a*	*a*	*a*	*a*	*a*	*a*
CH_3SSOH	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
$CH_3SS(=O)H$	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
$\bullet CH_2SSOH$	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			
$CH_3SS^{\bullet}{=}O$	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 $^{\bullet}CH_2SSOH$ has three internal rotors, while $CH_3SS^{\bullet}{=}O$ and $CH_3SS({=}O)H$ 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 H_3C—SS bond in CH_3SSOH, the H_3C—SS and CS—SO bonds in CH3SS$^{\bullet}$=O, H_3C—SS bond in $CH_3SS({=}O)H$ and the H_2C—SS bond in $^{\bullet}CH_2SSOH$ 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.

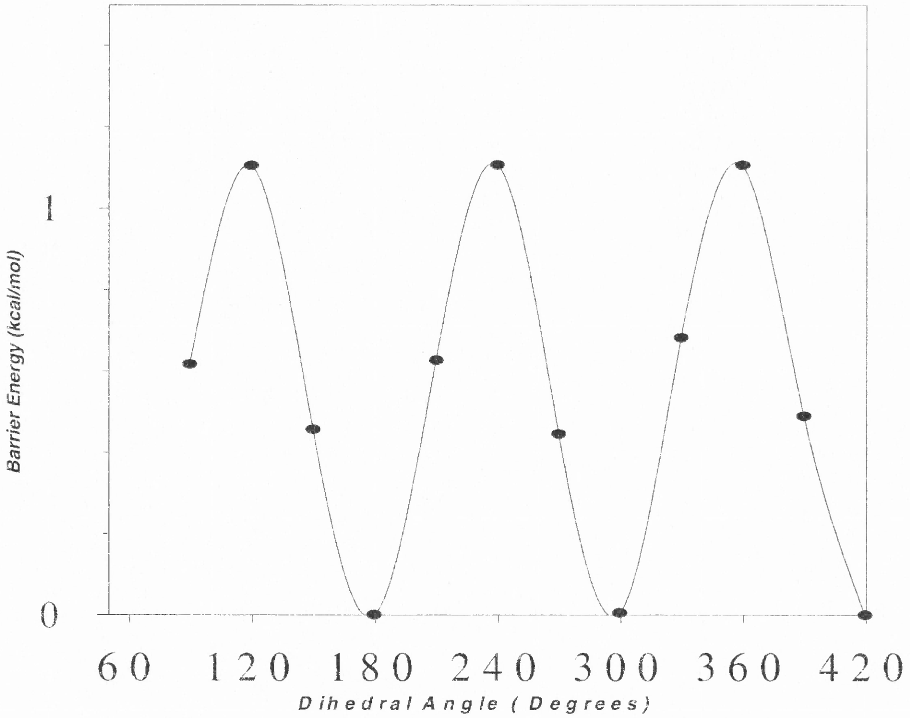


Figure 2.1 Potential energy profile for the H-C—S-(SOH) rotor in CH_3SSOH molecule

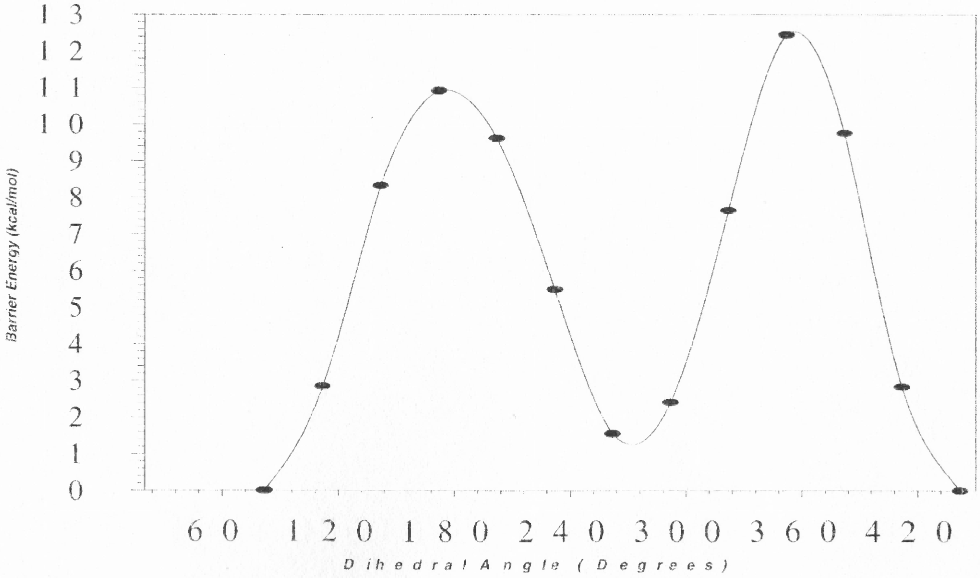


Figure 2.2 Potential energy profile for the $(CH_3)S$—$S(OH)$ rotor in CH_3SSOH molecule

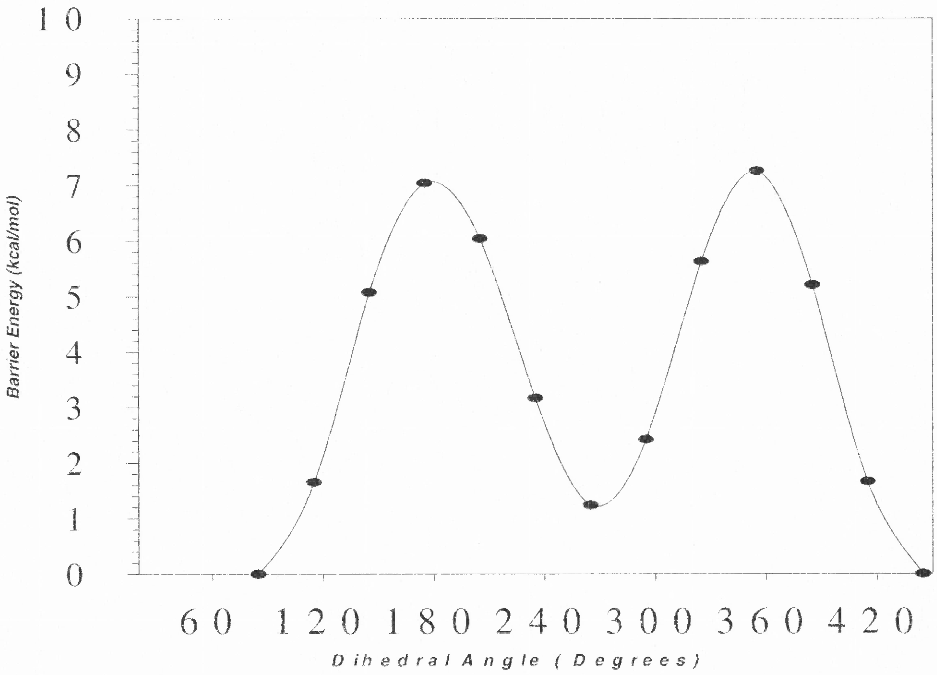


Figure 2.3 Potential energy profile for the $(CH_3)SS$—(OH) rotor in CH_3SSOH molecule

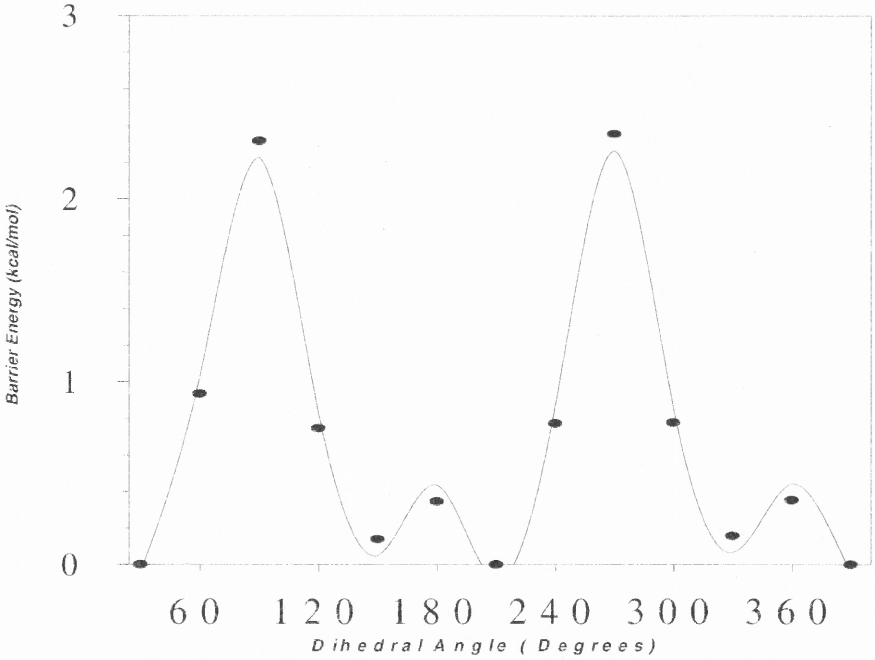


Figure 2.4 Potential energy profile for CH_2—S(SOH) rotor in $^{\bullet}CH_2SSOH$ molecule

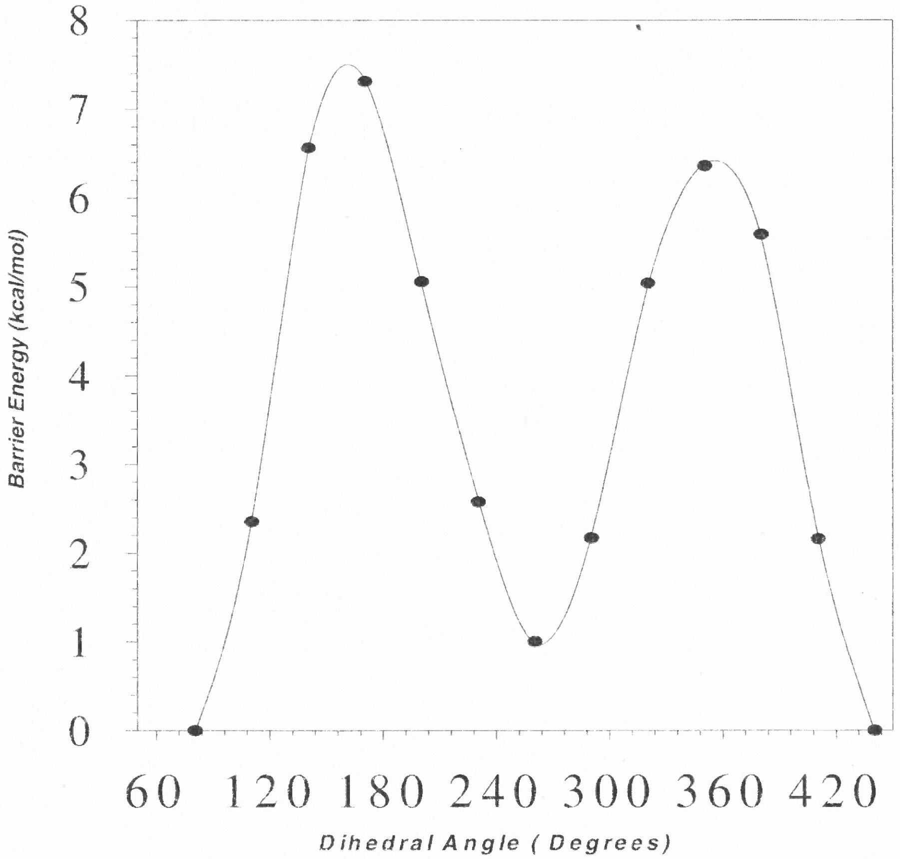


Figure 2.5 Potential energy profile for S—S rotor in $^{\bullet}CH_2S$--SOH molecule

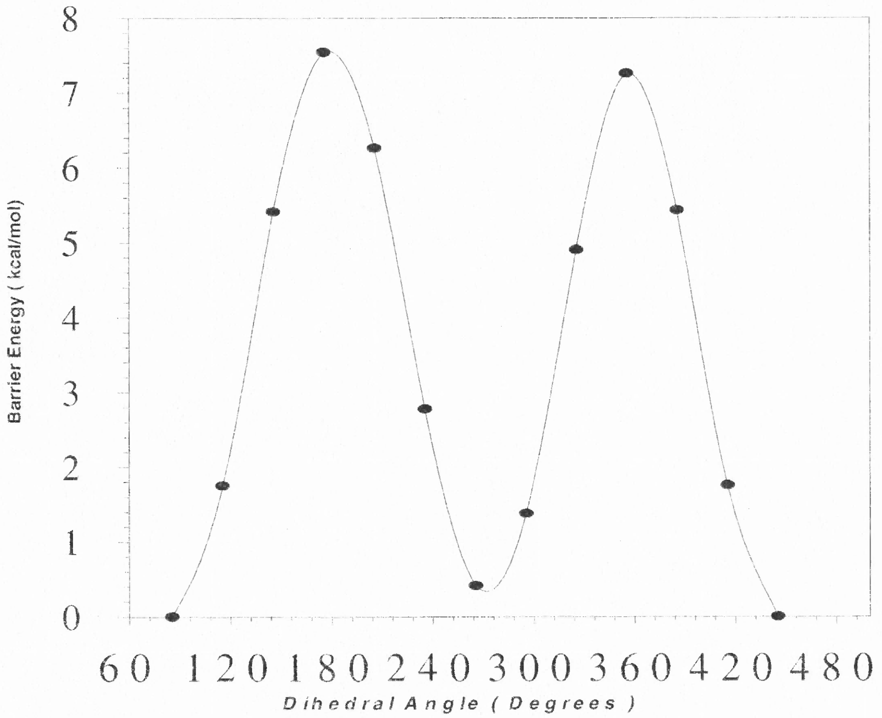


Figure 2.6 Potential energy profile for the CH_2S-S—O-H rotor in $^{\cdot}CH_2SSOH$ molecule

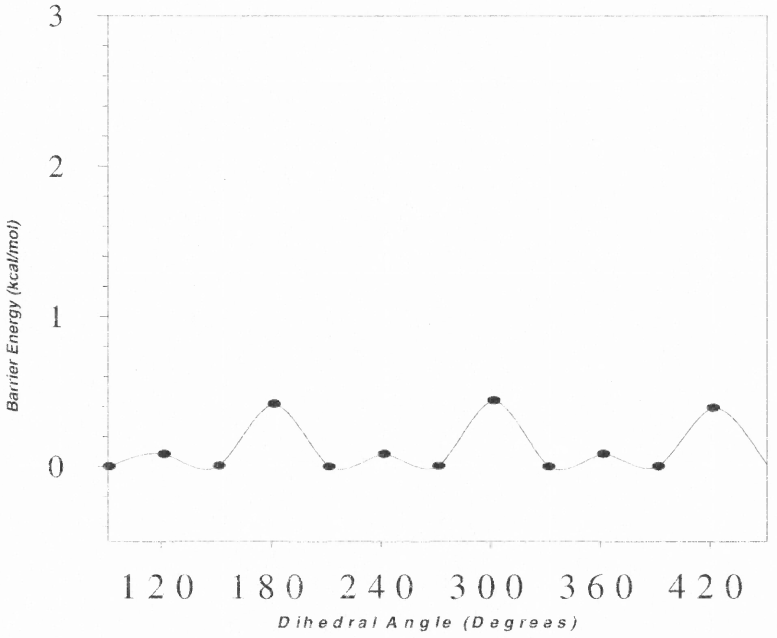
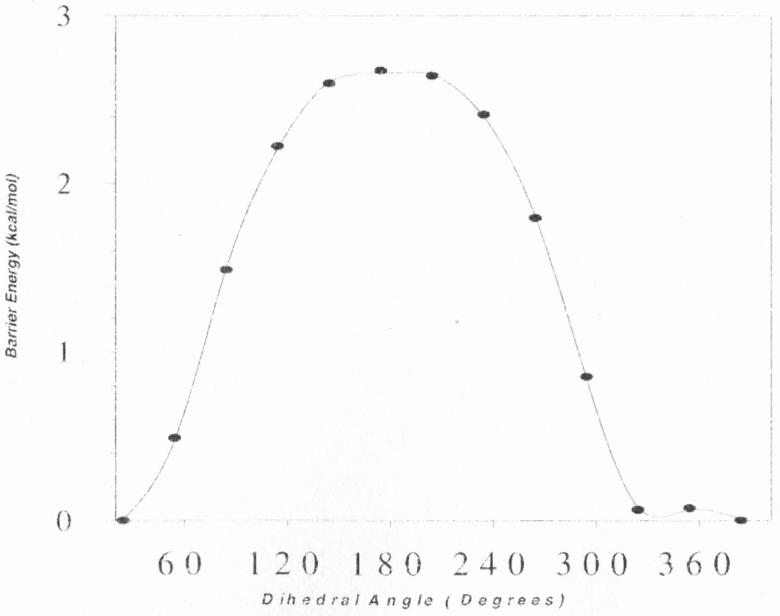


Figure 2.7 **Potential energy profile for the H_3C—$S(S^{\bullet}=O)$ rotor in CH_3--$SS^{\bullet}=O$.**



2.8 Potential energy profile for the CH_3-S—$S^{\bullet}=O$ rotor in $CH_3SS^{\bullet}=O$ molecule

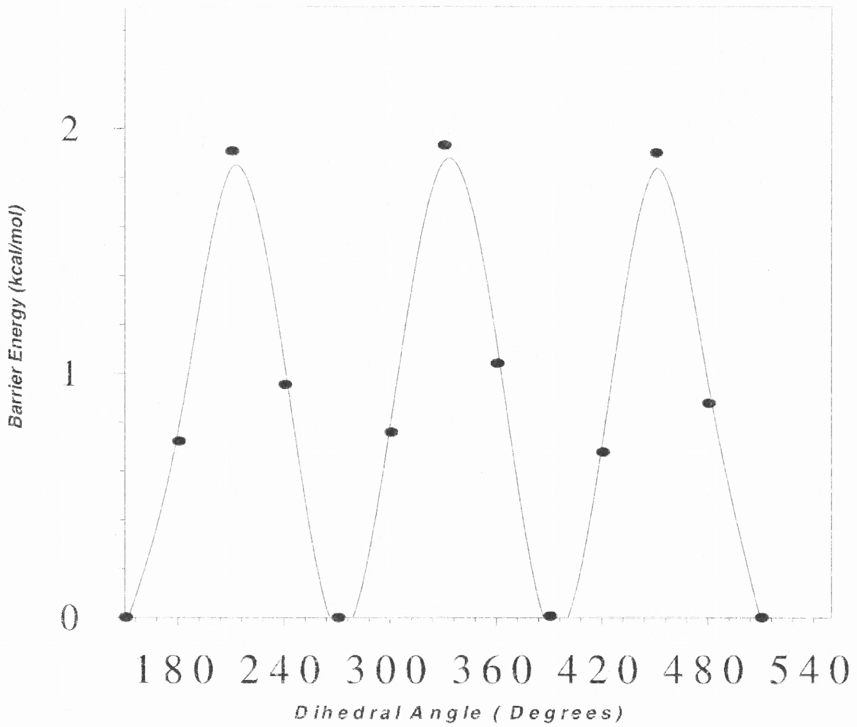


Figure 2.9 Potential energy profile for the H_3C—S-S(=O)H rotor in $CH_3SS(=O)H$ molecule

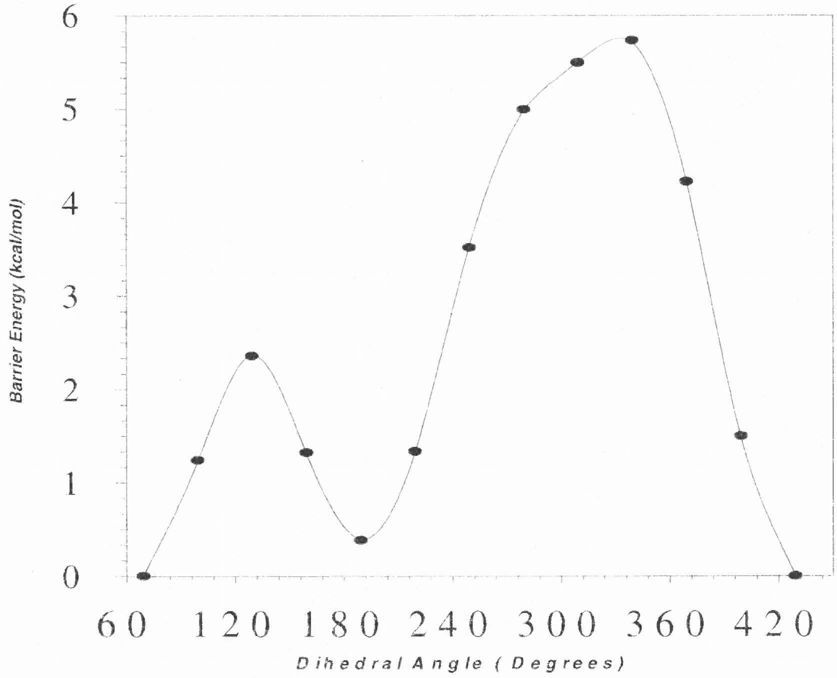


Figure 2.10 Potential energy profile for the H_3C-S—S(=O)H rotor in $CH_3SS(=O)H$ molecule

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 $CH_3SS.{=}O$ is also less than 3 kcal mol^{-1} due to minimum interaction between the methyl group and the O atom of S=O. The potential energy barrier for the S—S rotor in CH_3SSOH, $^{\cdot}CH_2SSOH$, and $CH_3SS(=O)H$ 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°298 and Cp°(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 ($S^o_{(298)}$) and Heat Capacity Cp(T)

Species	S^o298 cal mol^{-1} K^{-1}	Cp^o(T) (cal mol^{-1} K^{-1}) 300K	400K	500K	600K	800K	1000K	1500K
CH_3SSOH	74.26	20.58	23.51	25.93	27.91	30.93	33.20	36.93
**I.R Contribution*								
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
$CH_3SS(=O)H$	73.03	17.85	21.11	23.92	26.24	29.81	32.40	36.34
**I.R Contribution*								
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
$\bullet CH_2SSOH$	74.27	21.24	23.81	25.61	26.92	28.81	30.21	32.64
I.R Contribution								
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
$CH_3SS\bullet{=}O$	70.01	18.31	20.84	22.85	24.46	26.88	28.68	31.62
I.R Contribution								
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^o298 and $Cp^o(T)$ 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, $CH_3SS(=O)H$, $CH_3SS{\cdot}=O$ and $^{\cdot}CH_2SSOH$ 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 H—CH2SSOH, [CH3SSOH- [(H· + ·CH2SSOH)]] is 97.73 kcal mol-1. The O—H bond energy of CH3SSO—H [CH3SSOH- [(H· + CH3SS·=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 $CH_3SS(=O)H$, [$CH_3SS(=O)H$- [(H· + $\cdot CH_2SSOH$)]] is 77.01 kcal mol-1 . The S—H bond energy of $CH_3SS(=O)H$, [$CH_3SS(=O)H$- [(H· + $CH_3SS{\cdot}=O$)]] 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 (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]. 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 $[H, S_{n,\ O}]^{0/+/-}$[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 , $HSS^{\bullet}=O$ and $^{\bullet}SSOH$ 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 R_2S_2O or RHS_2O have low stability(s1) and we do not know of any compound of composition H_2S_2O being reported. There are however reports of thiosulfinates, RS(=O)SR where HS(=O)SH would be a direct corresponding structure from hydrogen substation 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 H2S2O, HRS2O and R2S2O have not been previously studied however there are ab ignition calculations at the HF and MP2 levels for H_2S_2O and Me_2S_2O (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 $HS^{\bullet}(=O)$ and $S^{\bullet}OH$ radicals and their cations and anions somewhat well known [24, 23]. Adams et al. have studied the $^{\bullet}SSOH$ 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 HSS•(=O) and $HOSS^{\bullet}$ 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 (HSS(=O)H) plus the radicals , $HSS^{\bullet}=O$ and $^{\bullet}SSOH$ and $^{\bullet}SS(=O)H$ 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 $S°298$ and $Cp°(T)$ 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 $S°298$ and $Cp°(T)$.

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$^{\bullet}$=O are 2.07 A°, 2.2 A° and 2.15 A^{0} 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 $^{\bullet}$SSOH is 1.69A°, while S—O bond distance in HSS$^{\bullet}$=O exhibits a shorter bond length of 1.51A°. In HSS(=O)H, the S—O bond is also similar to HSS$^{\bullet}$.=O at 1.49A°. The shorter S--O bond of 1.51A° of in HSS$^{\bullet}$=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)

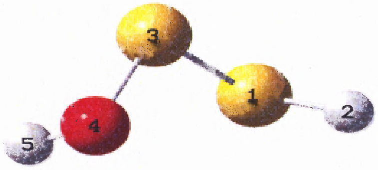
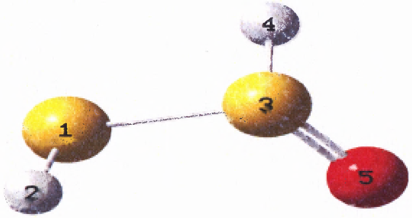
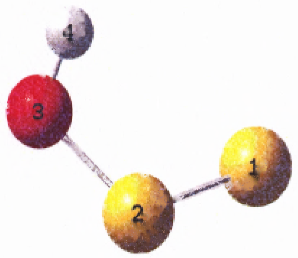
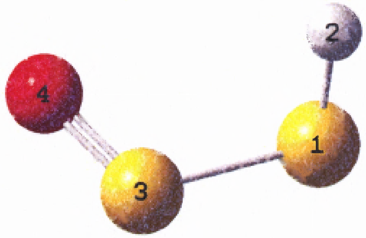
HSSOH			HSS(=O)H		
					
R1	R(1,2)	1.355	R1	R(1,2)	1.349
R2	R(1,3)	2.074	R2	R(1,3)	2.199
R3	R(3,4)	1.687	R3	R(3,4)	1.387
R4	R(4,5)	0.970	R4	R(3,5)	1.492
A1	A(2,1,3)	99.89	A1	A(2,1,3)	93.70
A2	A(1,3,4)	106.15	A2	A(1,3,4)	85.34
A3	A(3,4,5)	106.89	A3	A(1,3,5)	114.05
D1	D(2,1,3,4)	-84.01	A4	A(4,3,5)	108.74
D2	D(1,3,4,5)	-85.50	D1	D(2,1,3,4)	-164.28
			D2	D(2,1,3,5)	87.26

Table 3.1 continued





$^{\bullet}$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$^{\bullet}$(=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$^{\bullet}$=O		$^{\bullet}$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$\cdot$=O and $^{\bullet}$SSOH respectively. The enthalpy calculations are based on the lowest energy conformer.

Work reactions for HSSOH:

$HSSOH \quad C_2H_6 \rightarrow HSSH + CH_3CH_2OH$ (1)

$HSSOH + C_2H_6 \rightarrow HSCH_3 + CH_3SOH$ (2)

$HSSOH + CH_4 \rightarrow HSH + CH_3SOH$ (3)

$HSSOH + CH_3SH \rightarrow CH_3SSH + HSOH$ (4)

$HSSOH + HSH \rightarrow HSSH + HSOH$ (5)

$HSSOH + CH_3SCH_3 \rightarrow CH_3SSCH_3 + HSOH$ (6)

Work reactions for HSS(=O)H:

$HSS(=O)H + C_2H_6 \rightarrow CH_3S(=O)H + CH_3SH$ (7)

$HSS(=O)H + CH_4 \rightarrow HSH + CH_3S(=O)H$ (8)

$HSS(=O)H + CH_3SOH \rightarrow CH_3S(=O)H + HSSOH$ (9)

Work reactions for HSS$^{\bullet}$=O:

$HSS{\cdot}{=}O + CH_3OH \rightarrow HSSOH + CH_3O^{\cdot}$ (10)

$HSS{\cdot}{=}O + C_2H_5OH \rightarrow HSSOH + C_2H_5O^{\cdot}$ (11)

$HSS{\cdot}{=}O + CH_3SOH \rightarrow HSSOH + CH_3S^{\cdot}{=}O$ (12)

$HSS^{\cdot}{=}O + HSH \rightarrow HSSH + HS^{\cdot}{=}O$ (13)

$HSS^{\cdot}{=}O + CH_3S\ CH_3 \rightarrow CH_3SSCH_3 + HS^{\cdot}{=}O$ (14)

Work reactions for $^{\cdot}SSOH$

$^{\cdot}SSOH + CH_3SH \rightarrow HSSOH + {}^{\cdot}CH_2SH$ (15)

$^{\cdot}SSOH + C_2H_5SH \rightarrow HSSOH + CH_3\ {}^{\cdot}CHSH$ (16)

$^{\cdot}SSOH + CH_3SCH_3 \rightarrow HSSOH + {}^{\cdot}CH_2SCH_3$ (17)

$^{\cdot}SSOH + CH_3SH \rightarrow HSSOH + CH_3SH$ (18)

$^{\cdot}SSOH + HSH \rightarrow HSSOH + {}^{\cdot}SH$ (19)

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 $\Delta H_{rxn(298)}$ (kcal mol^{-1}) from isodesmic reactions

Isodesmic reaction	B3LYP/6-311G (d, p)	B3LYP/6-311G (3df, 2p)	CBSQB3
Work reactions for HSSOH:			
$HSSOH\ C_2H_6 \rightarrow HSSH + CH_3CH_2OH$	-2.48	-0.848	0.966
$HSSOH + C_2H_6 \rightarrow HSCH_3 + CH_3SOH$	11.24	12.93	11.86
$HSSOH + CH_4 \rightarrow HSH + CH_3SOH$	9.98	11.32	10.11
$HSSOH + CH_3SH \rightarrow CH3SSH + HSOH$	15.79	16.05	9.69
$HSSOH + HSH \rightarrow HSSH + HSOH$	19.23	19.35	19.35
$HSSOH + CH_3SCH_3 \rightarrow CH_3SSCH_3 + HSOH$	14.87	14.69	13.62
Work reactions for HSS(=O)H:			
$HSS(=O)H + C_2H_6 \rightarrow CH_3S(=O)H + CH_3SH$	5.64	7.27	6.27
$HSS(=O)H + CH_4 \rightarrow HSH + CH_3S(=O)H$	4.38	5.66	4.52
$HSS(=O)H + CH_3OH \rightarrow CH_3S(=O)H + HSOH$	-5.59	-5.65	-5.58
Work reactions for HSS·=O:			
$HSS{\cdot}{=}O + CH_3OH \rightarrow HSSOH + CH_3O^{\cdot}$	24.77	30.17	34.35
$HSS{\cdot}{=}O + C_2H_5OH \rightarrow HSSOH + C_2H_5O^{\cdot}$	26.89	32.43	33.83
$HSS{\cdot}{=}O + CH_3SOH \rightarrow HSSOH + CH_3S{\bullet}{=}O$	-6.19	-5.94	-5.50
$HSS{\cdot}{=}O + HSH \rightarrow HSSH + HS^{\cdot}{=}O$	16.99	24.25	17.85
$HSS{\cdot}{=}O + CH_3S\ CH_3 \rightarrow CH_3SSCH_3 + HS^{\cdot}{=}O$	12.63	19.59	12.12
Work reactions for ·SSOH			
$^{\cdot}SSOH + CH_3SH \rightarrow HSSOH + {}^{\cdot}CH_2SH$	30.27	28.15	29.32
$^{\cdot}SSOH + C_2H_5SH \rightarrow HSSOH + CH_3\,{}^{\cdot}CHSH$	27.38	25.91	27.83
$^{\cdot}SSOH + CH_3SCH_3 \rightarrow HSSOH + {}^{\cdot}CH_2SCH_3$	29.07	23.63	28.37
$^{\cdot}SSOH + CH_3SH \rightarrow HSSOH + CH_3SH$	17.40	19.65	20.78
$^{\cdot}SSOH + HSH \rightarrow HSSOH + {}^{\cdot}SH$	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 ΔHf(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
Enthalpies of Formation of HSSOH:			
$HSSOH\ C_2H_6 \rightarrow HSSH + CH_3CH_2OH$	-28.85	-30.49	-32.30
$HSSOH + C_2H_6 \rightarrow HSCH_3 + CH_3SOH$	-29.80	-31.49	-30.43
$HSSOH + CH_4 \rightarrow HSH + CH_3SOH$	-30.88	-32.23	-31.02
$HSSOH + CH_3SH \rightarrow CH3SSH + HSOH$	-38.76	-39.02	-32.66
$HSSOH + HSH \rightarrow HSSH + HSOH$	- 37.55	- 37.68	- 37.67
$HSSOH + CH_3SCH_3 \rightarrow CH_3SSCH_3 + HSOH$	-38.88	- 38.70	- 37.63
Average	- 34.12	- 34.94	**- 33.62**
Mean of averages	***-34.23***		
Enthalpies of Formation of HSS(=O)H:			
$HSS(=O)H + C_2H_6 \rightarrow CH_3S(=O)H + CH_3SH$	-10.91	-12.54	-11.54
$HSS(=O)H + CH_4 \rightarrow HSH + CH_3S(=O)H$	-11.99	-13.27	-12.13
$HSS(=O)H + CH_3SOH \rightarrow CH_3S(=O)H + HSSOH$	-14.98	-14.93	-14.99
	-12.62	**-13.58**	**-12.88**
Mean of averages	***-13.03***		
Enthalpies of Formation of HSS·=O:			
$HSS^{\bullet}{=}O + CH_3OH \rightarrow HSSOH + CH_3O^{\bullet}$	-6.52	-11.91	-16.09
$HSS^{\bullet}{=}O + C_2H_5OH \rightarrow HSSOH + C_2H_5O^{\bullet}$	-8.56	-14.09	-15.44
$HSS^{\bullet}{=}O + CH_3SOH \rightarrow HSSOH + CH_3S{=}O$	-12.09	-12.35	-12.78
$HSS^{\bullet}{=}O + HSH \rightarrow HSSH + HS^{\bullet}{=}O$	-13.12	- 20.37	- 13.97
$HSS^{\bullet}{=}O + CH_3S\ CH_3 \rightarrow CH_3SSCH_3 + HS^{\bullet}{=}O$	-14.44	-21.40	- 13.93
Average	**-10.94**	**-16.02**	**-14.44**
Mean of averages*	***-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 ${}^{\cdot}SSOH$			
${}^{\cdot}SSOH + CH_3SH \rightarrow HSSOH + {}^{\cdot}CH_2SH$	-20.97	-18.86	-20.03
${}^{\cdot}SSOH + C_2H_5SH \rightarrow HSSOH + CH_3\,{}^{\cdot}CHSH$	-19.59	-18.12	-20.04
${}^{\cdot}SSOH + CH_3SCH_3 \rightarrow HSSOH + {}^{\cdot}CH_2SCH_3$	-20.23	-17.79	-19.24
${}^{\cdot}SSOH + CH_3SH \rightarrow HSSOH + CH_3SH$	- 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^{o}_{f298}	Species	ΔH^{o}_{f298}
H [11]	52.1	C_2H_6 [17]	-20.04
CH_4 [16]	-17.89	HSSH [28]	3.98
CH_3SCH_3 [11]	-8.94	CH_3SH [20]	-5.47
C_2H_5OH [19]	-56.17	CH_3SOH [14]	-33.9
C_2H_5SH [12]	-10.99	CH_3OH [19]	-48.04
${}^{\cdot}CH_2SCH_3$ [12]	33.78	$CH_3\,{}^{\cdot}CHSH$	30.64
${}^{\cdot}CH_2SH$ [13]	37.7	$CH_3SO^{\cdot}$ [13]	18.31
$C_2H_5O^{\cdot}$ [28]	-3. 9	$CH_3O^{\cdot}$.[18]	4.1
$CH_3S(=O)H$ [21]	-20.6	HSH [22]	-4.9
HSOH [22]	-27.2	$CH3O^{\cdot}$ [28]	4.1
$HS^{\cdot}=O$ [28]	-5.0	CH3SSCH3 [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$^{\cdot}$ + $^{\cdot}$SSOH)]] reaction and the bond energy of O—H in HSSOH is calculated using [HSSOH- [(H$^{\cdot}$ + HSSO$^{\cdot}$)]]. Similarly, the Bond Energy of S—H bond in H—SS(=O)H is calculated using [HSS(=O)H- [(H$^{\cdot}$ + $^{\cdot}$SSOH)]] reaction and the bond energy of S—H in HSS(O) —H is calculated using [HSS(=O)H- [(H$^{\cdot}$ + HSS$^{\cdot}$=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

	Moment of Inertia, units amu(Bohr)^2			frequencies (cm^{-})		
Species	*I 1*	*I 2*	*I 3*	*a*	*a*	*a*
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
$^{\bullet}$SSOH	73.90734	386.61948	457.28657	113.768	289.140	619.197
				(716.891)	1138.732	3740.530
HSS$^{\bullet}$=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 $^{\bullet}$SSOH and HSS$^{\bullet}$=O have only one rotor each, $^{\bullet}$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 $^{\bullet}$SS—OH rotor has only one barrier at 2.45 with a second very small barrier at 0.1 kcal mol^{-1}. The HS—S(=O)H rotor has two fold potential with barriers are 1.75 and 0.8 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^{-}. Rotations about The HS--S$^{\bullet}$=O rotor and $^{\bullet}$SS--OH rotor have energy barriers less than 3.0 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.

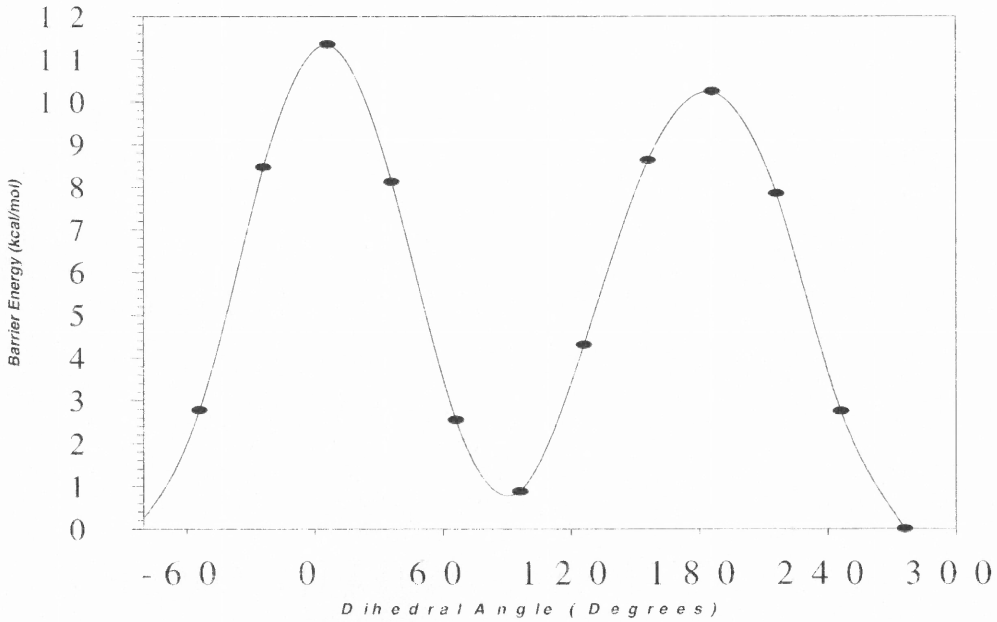


Figure 3.1 Potential energy profile for the HS—SOH) rotor in HSSOH molecule

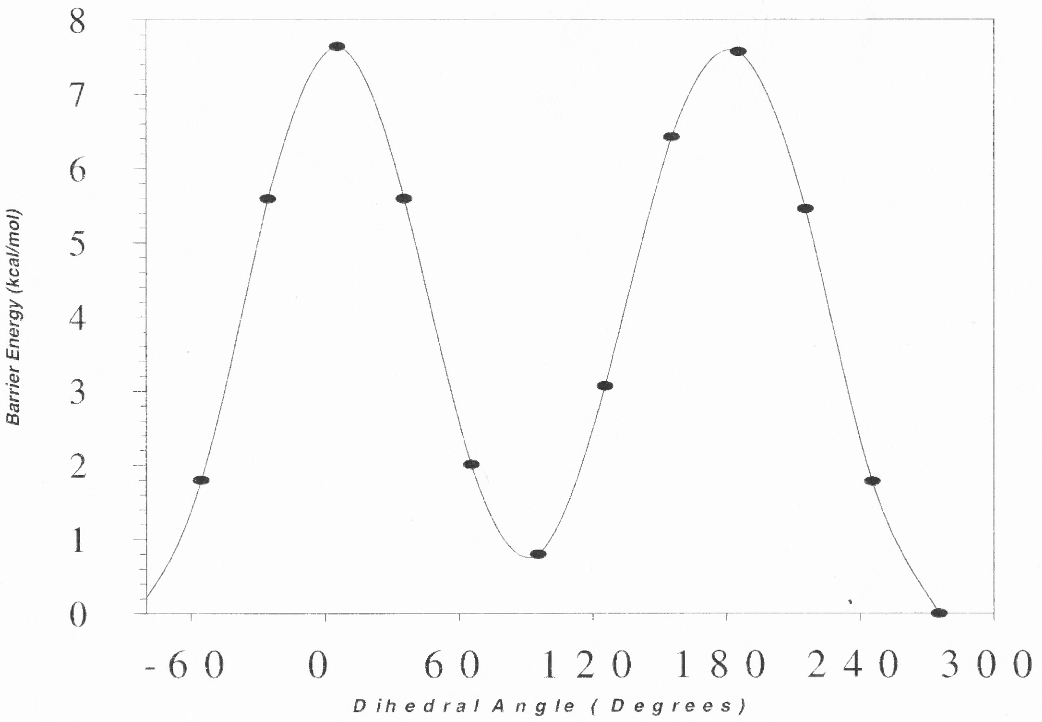


Figure 3.2 Potential energy profile for the HSS—OH rotor in HSSOH molecule

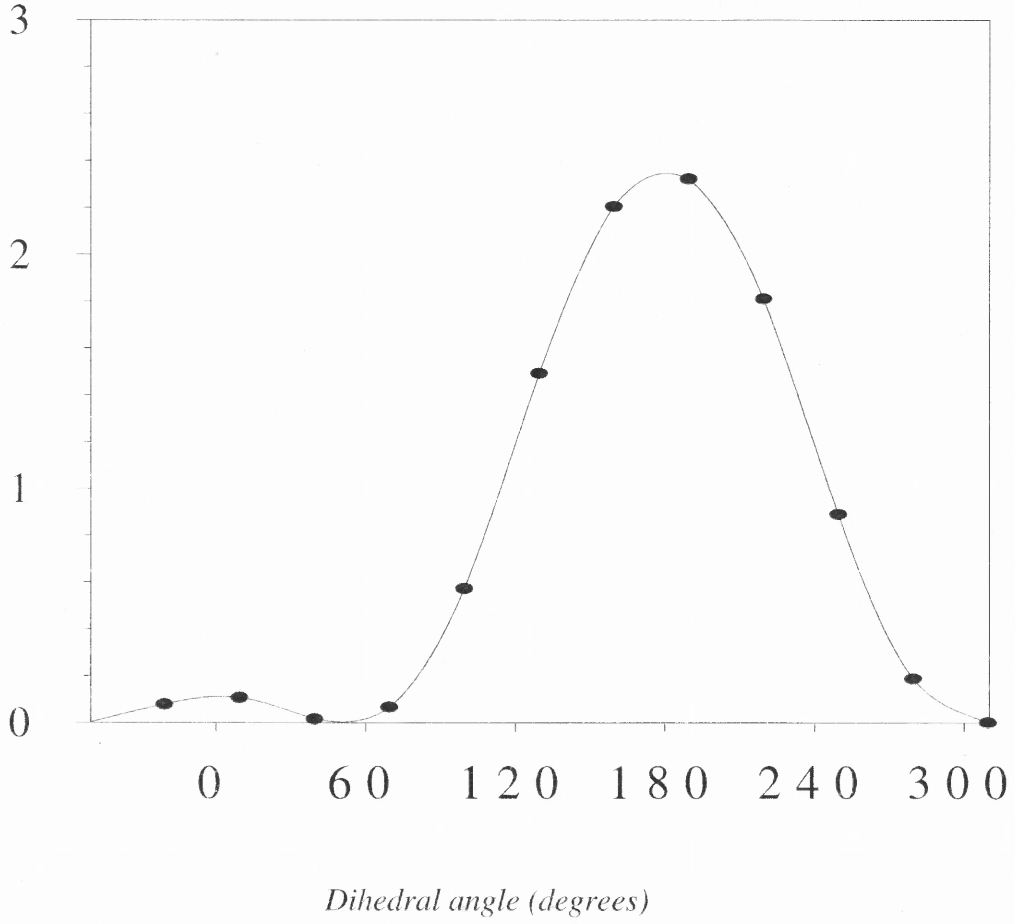


Figure 3.3 Potential energy profile for S-S—O-H rotor in ˙SSOH molecule

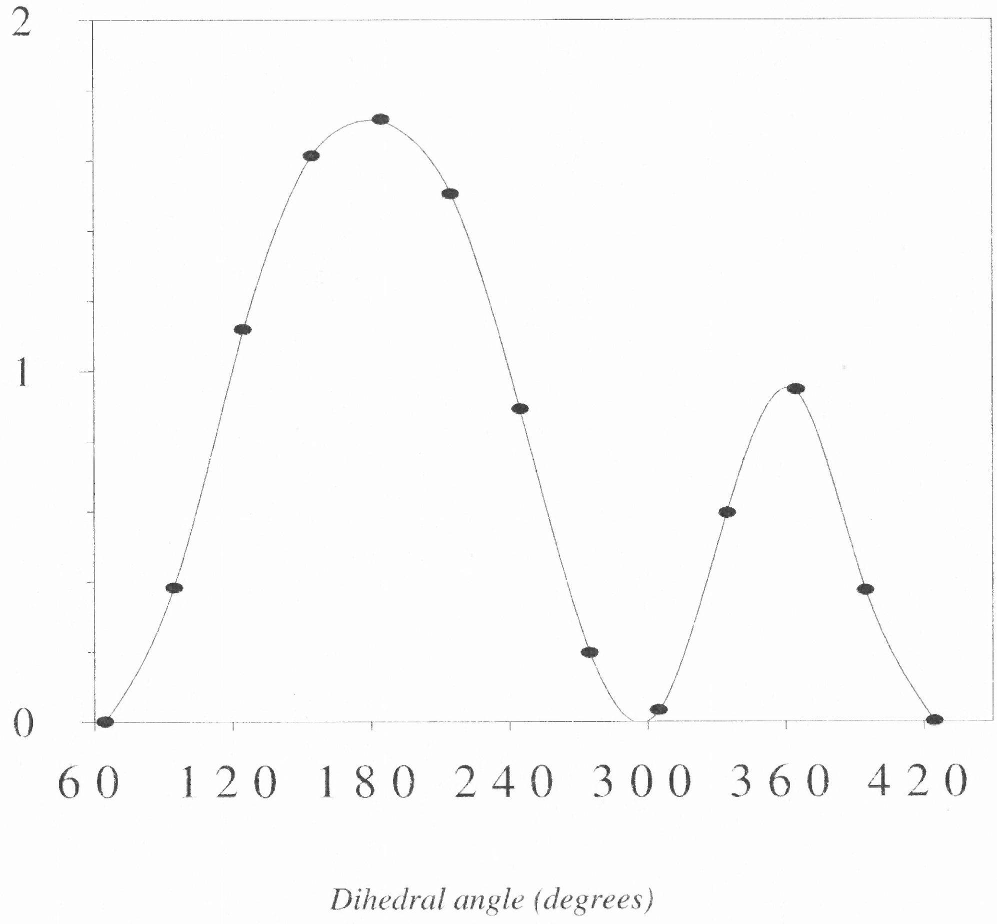


Figure 3.4 Potential energy profile for the HS— S$^\bullet$=O rotor in H--SS$^\bullet$=O

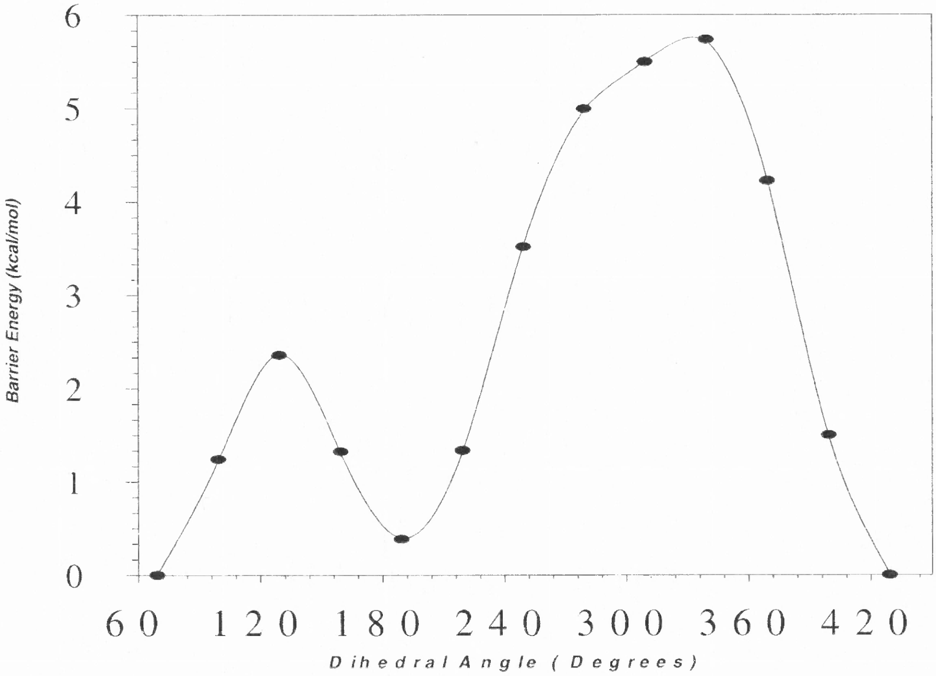


Figure 3.5 Potential energy profile for the H-S—S(=O)H rotor in HSS(=O)H molecule

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°298 and Cp°(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 Cp(T) paramters 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 ($S^{o}_{(298)}$) and Heat Capacity Cp(T)

		Cp°(T) (cal mol^{-1} K^{-1})						
Species	S°298 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.R Contribution								
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.R Contribution								
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.R Contribution								
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.R Contribution								
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 _Cp_°(_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 ·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$^{\bullet}$=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 $^{\bullet}$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$^{\bullet}$=O radical.

CHAPTER 4

STRUCTURAL AND THERMOCHEMICAL STUDIES ON S-S-O BRIDGED SYSTEM IN CH_3SSOCH_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 ($CH_3S\bullet$) with $^3O_2$ 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 $CH_3S + O_2 \leftrightarrow CH_3S\text{-}OO$ reaction has a very shallow well, ~ 10 kcal mol^{-1}, which results in a very rapid reverse reaction to back to $CH_3S^\bullet$ and a quasi equilibrium. The CH_3S and CH_3SOO can react with hydroperoxides (e.g. HO_2, CH_3SOO.) or OH or NOx to form the CH_3SO moiety, which exists as $CH_3S^\bullet(=O)$.

$CH_3S^\bullet{=}O$ 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 $CH_3S\bullet{=}O$ radical with O_2, NO_2, and O_3 as well as the thermal decomposition of $CH_3\text{-}SO_2$ [5].

It has been shown that the $CH_3SS\bullet{=}O$ radical can be formed by the reaction $CH_3SS + NO_2 \rightarrow CH_3SS\bullet{=}O + NO$ and $CH_3SS\bullet{=}O$ 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_3SSOCH_3 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 CH_3SSOCH_3, 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 CH_3SSOCH_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 Cp° (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 Cp° (T).

4.3 Results and Discussion

4.3.1 Structure

The S—O bond distance in CH3SSOCH3 is 1.69 A° and 1.68 A° in $^{\cdot}$CH2SSOCH3 and 1.71 A° in CH3SSOC$^{\cdot}$H2.

The C—S bond in CH3SSOCH3 and CH3SSOC$^{\cdot}$H2 is 1.83 A° against the 1.73A° in $^{\cdot}$CH2SSOCH3. The C—O bond distance in CH3SSOCH3 and $^{\cdot}$CH2SSOCH3 is 1.43 A° and 1.36 A°, slightly shorter in CH3SSOC$^{\cdot}$H2.

The formation of $^{\cdot}CH_2SSOCH_3$ is accompanied by reduction of the O-C-H bond angle to 107.15 °,while formation of $CH_3SSOC{\cdot}H_2$ reveals increase in bond angle O-C-H to 118.90 ° compared to the O-C-H bond angle of 111.47 ° in CH_3SSOCH_3 as listed in Table 4.1.

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

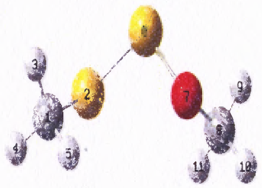
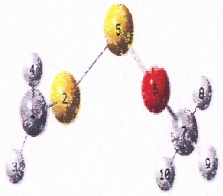
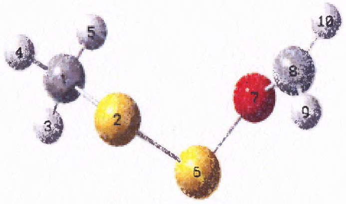
CH_3SSOCH_3		$^{\cdot}CH_2SSOCH_3$		$CH_3SSOC\cdot H_2$	
					
R(1,2)	1.839	R(1,2)	1.728	R(1,2)	1.83
R(1,3)	1.090	R(1,3)	1.08	R(1,3)	1.09
R(1,4)	1.093	R(1,4)	1.08	R(1,4)	1.09
R(1,5)	1.090	R(2,5)	2.09	R(1,5)	1.09
R(2,6)	2.060	R(5,6)	1.68	R(2,6)	2.05
R(6,7)	1.690	R(6,7)	1.43	R(6,7)	1.71
R(7,8)	1.433	R(7,8)	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_3SSOCH_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
$^{\bullet}CH_2SSO\ CH_3$			
	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_3SSOCH_3		$^{\bullet}CH_2SSOCH_3$	
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 CH_3SSOCH_3 and its radical, $^{\bullet}CH_2SSOCH_3$. The enthalpy calculations are based on the lowest energy conformer.

Work reactions CH_3SSOCH_3:

$CH_3SSOCH_3 + C_2H_6 \rightarrow CH_3SSCH_3 + CH_3CH_2OH$ (1)

$CH_3SSOCH_3 + C_2H_6 \rightarrow CH_3SC_2H_5 + CH_3SOH$ (2)

$CH_3SSOCH_3 + CH_4 \rightarrow CH_3SCH_3 + CH_3SOH$ (3)

Work reactions for $^{\bullet}CH_2SSOCH_3$:

$^{\bullet}CH_2SSOCH_3 + CH_3SH \rightarrow CH_3SSOCH_3 + {^{\bullet}CH_2SH}$ (4)

$^{\bullet}CH_2SSOCH_3 + C_2H_5SH \rightarrow CH_3SSOCH_3 + CH_3C^{\bullet}HSH$ (5)

$^{\bullet}CH_2SSOCH_3 + CH_3SCH_3 \rightarrow CH_3SSOCH_3 + {^{\bullet}CH_2SCH_3}$ (6)

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 ΔH_{rxn298} (kcal mol-1) from isodesmic reactions

Isodesmic reaction	B3LYP/6-31G (d, p)	B3LYP/6-311++G (3df, 2p)	CBSQB3
Work reactions for CH_3SSOCH_3:			
$CH_3SSOCH_3 + C_2H_6 \rightarrow CH_3SS\,CH_3 + CH_3CH_2OH$	-8.11	-7.77	-6.20
$CH_3SSOCH_3 + C_2H_6 \rightarrow CH_3SC_2H_5 + CH_3SOH$	6.96	6.99	5.41
$CH_3SSOCH_3 + CH_4 \rightarrow CH_3S\,CH_3 + CH_3SOH$	8.71	9.06	8.67
Work reactions for $\cdot CH_2SSOCH_3$:			
$\cdot CH_2SSOCH_3 + CH_3SH \rightarrow CH_3SSOCH_3 + {}^{\cdot}CH_2SH$	- 1.32	-1.82	-2.33
$\cdot CH_2SSOCH_3 + C_2H_5SH \rightarrow CH_3SSOCH_3 + CH_3C^{\cdot}HSH$	-4.21	-4.06	-3.82
$\cdot CH_2SSOCH_3 + CH_3S\,CH_3 \rightarrow CH_3SSOCH_3 + {}^{\cdot}CH_2SCH_3$	-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
Enthalpies of Formation of CH_3SSOCH_3:			
$CH_3SSOCH_3 + C_2H_6 \rightarrow CH_3SSCH_3 + CH_3CH_2OH$	-32.97	-33.31	-35.68
$CH_3SSOCH_3 + C_2H_6 \rightarrow CH_3SC_2H_5 + CH_3SOH$	-34.48	-34.51	-33.69
$CH_3SSOCH_3 + CH_4 \rightarrow CH_3SCH_3 + CH_3SOH$	-33.66	-34.01	- 33.62
Average	-33.70	-33.94	**- 34.33**
Mean of averages	***-33.99***		
Enthalpies of Formation of $\cdot CH_2SSOCH_3$:			
$\cdot CH_2SSOCH_3 + CH_3SH \rightarrow CH_3SSOCH_3 + {}^{\cdot}CH_2SH$	10.79	11.05	11.17
$\cdot CH_2SSOCH_3 + C_2H_5SH \rightarrow CH_3SSOCH_3 + CH_3C^{\cdot}HSH$	12.18	11.78	11.16
$\cdot CH_2SSOCH_3 + CH_3SCH_3 \rightarrow CH_3SSOCH_3 + {}^{\cdot}CH_2SCH_3$	11.54	12.12	11.97
Average	11.50	11.65	**11.44**
Mean of averages	***11.53***		

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

Species	ΔH^o_{f298}	Species	ΔH^o_{f298}
H [11]	52.1	C_2H_6 [17]	-20.04
CH_4 [16]	-17.89	CH_3SCH_3 [11]	-8.94
CH_3SH [20]	-5.47	C_2H_5OH [19]	-56.17
CH_3SOH [14]	-33.9	C_2H_5SH [12]	-10.99
CH_3OH [19]	-48.04	$^{\bullet}CH_2SCH_3$ [12]	33.78
$CH_3\ {}^{\bullet}CHSH$ [28]	30.64	$^{\bullet}CH_2SH$ [3]	37.7
CH_3SSOCH_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—CH_2SSOCH_3 is calculated using [CH_3SSOCH_3- [($H^{\cdot}$ + $^{\cdot}CH_2SSOCH_3$)]] 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
CH_3SSOCH_3:				
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

	Moment of Inertia, units amu(Bohr)^2			frequencies (cm^{-})					
Species	*I 1*	*I 2*	*I 3*	*a*	*a*	*a*	*a*	*a*	*a*
CH_3SSOCH_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			
$\bullet CH_2SSOCH_3$	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 CH_3SSOCH_3 and corresponding methyl radical ${}^{\cdot}CH_2SSOCH_3$ has four internal rotors. While $CH_3SSOC{\bullet}H_2$ falls apart to $CH_3S{=}O$ 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 H_3C—SS and SO—CH_3 bond in CH_3SSOCH_3, the H_3C—SS and SO—CH_3 bonds in ${}^{\cdot}CH_2SSOCH_3$, have energy barriers less than 3.0 kcal.

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

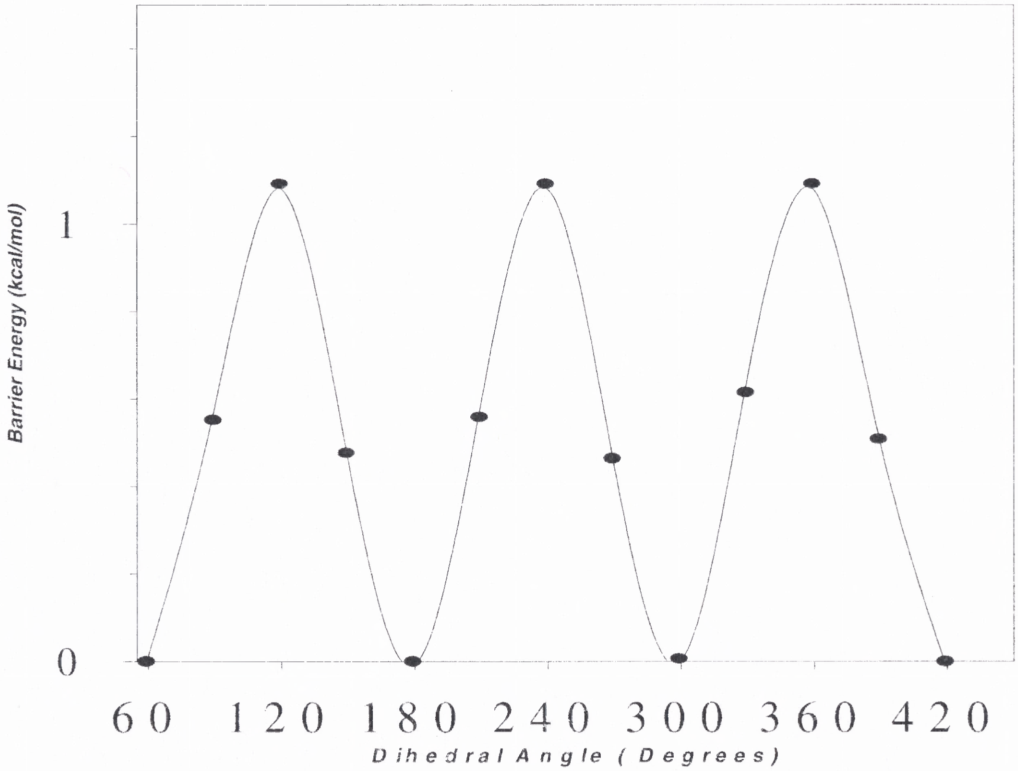


Figure 4.1 Potential energy profile for the H-C—S-(SOC) rotor in CH_3SSOCH_3 molecule

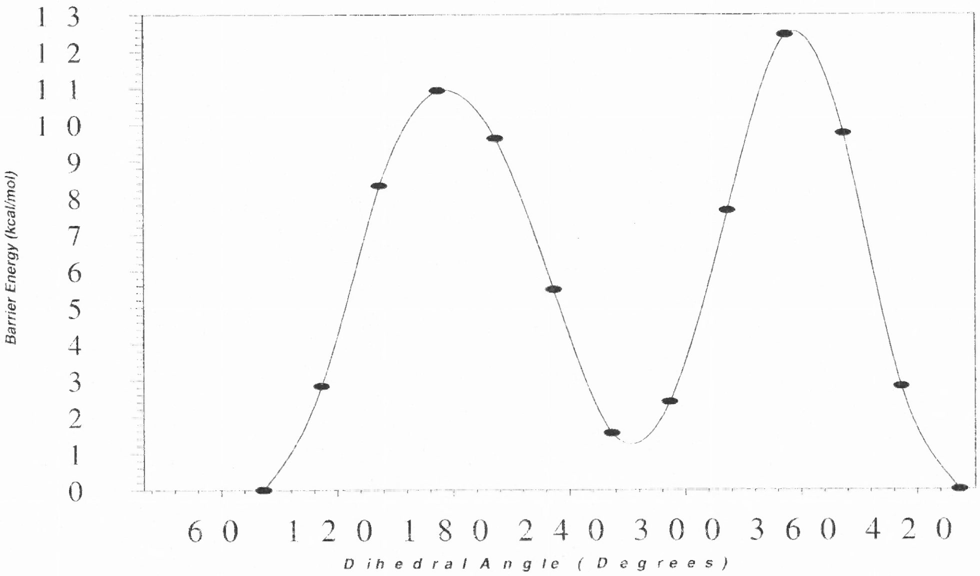


Figure 4.2 Potential energy profile for the (CH3)S—S(OH) rotor in CH_3SSOCH_3H molecule

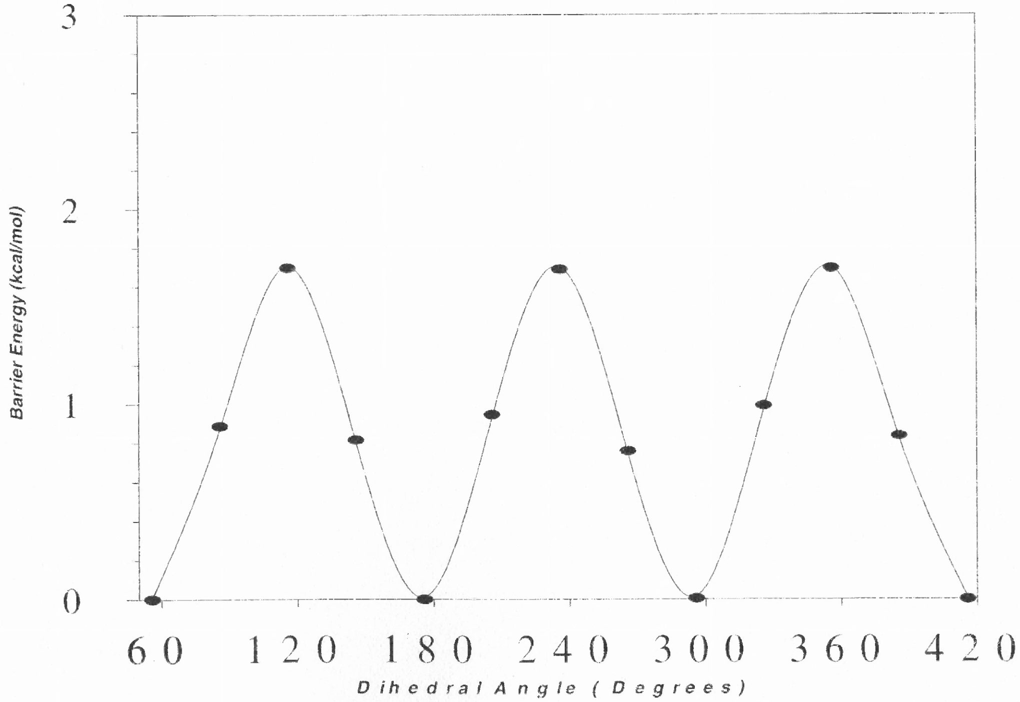


Figure 4.3 Potential energy profile for the (CH_3SS O—C) rotor in CH_3SSOCH_3 molecule

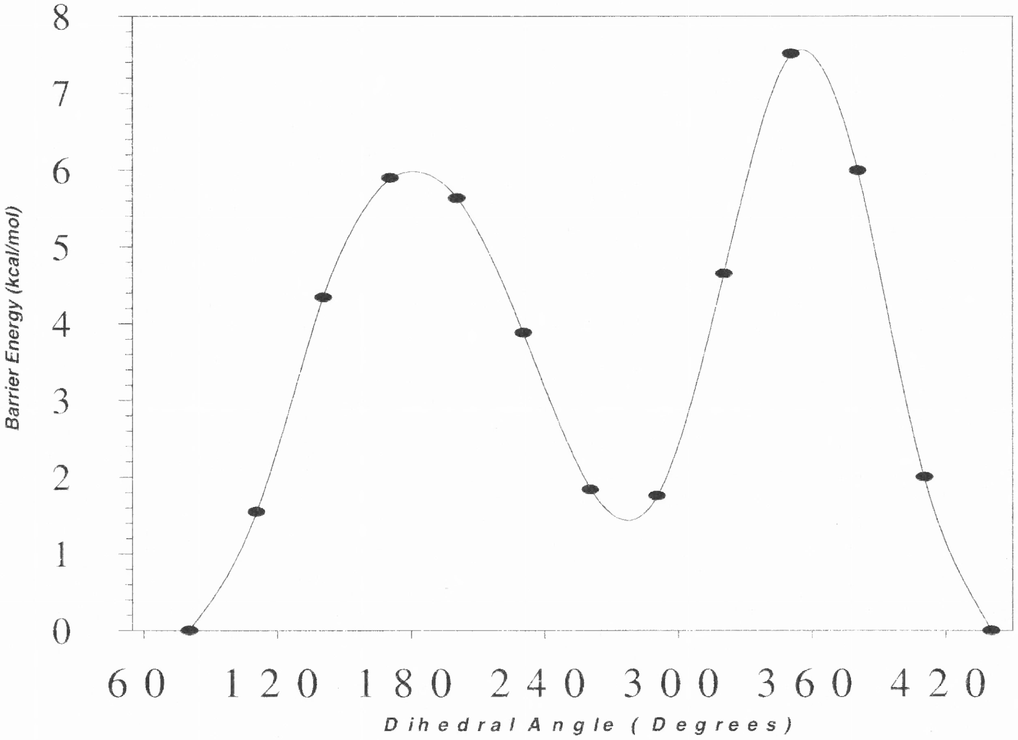


Figure 4.4 Potential energy profile for $CH_3S(S—OC)$ rotor in CH_3SSOCH_3 molecule

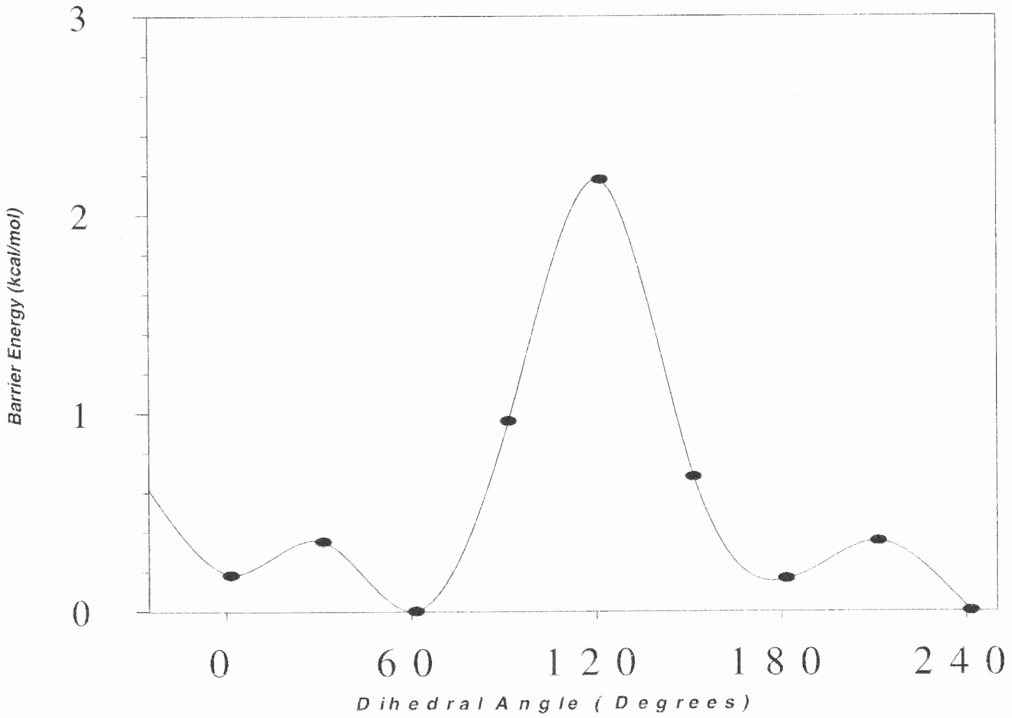


Figure 4.5 Potential energy profile for C—S rotor in $^{\bullet}CH_2$—SSOC molecule

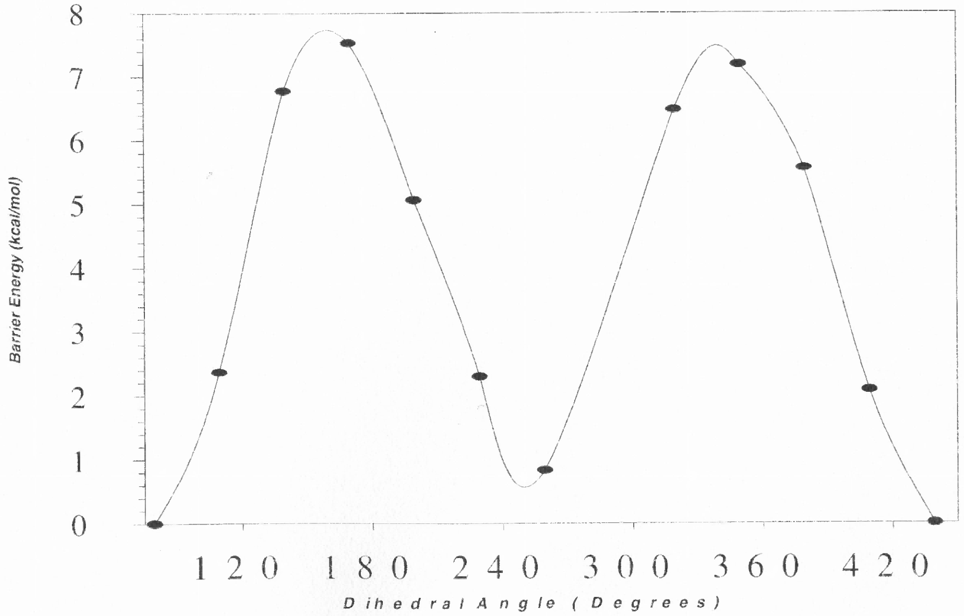


Figure 4.6 Potential energy profile for the $^{\cdot}$CH2S—SO-C rotor in $^{\cdot}CH_2SSOCH_3$ molecule

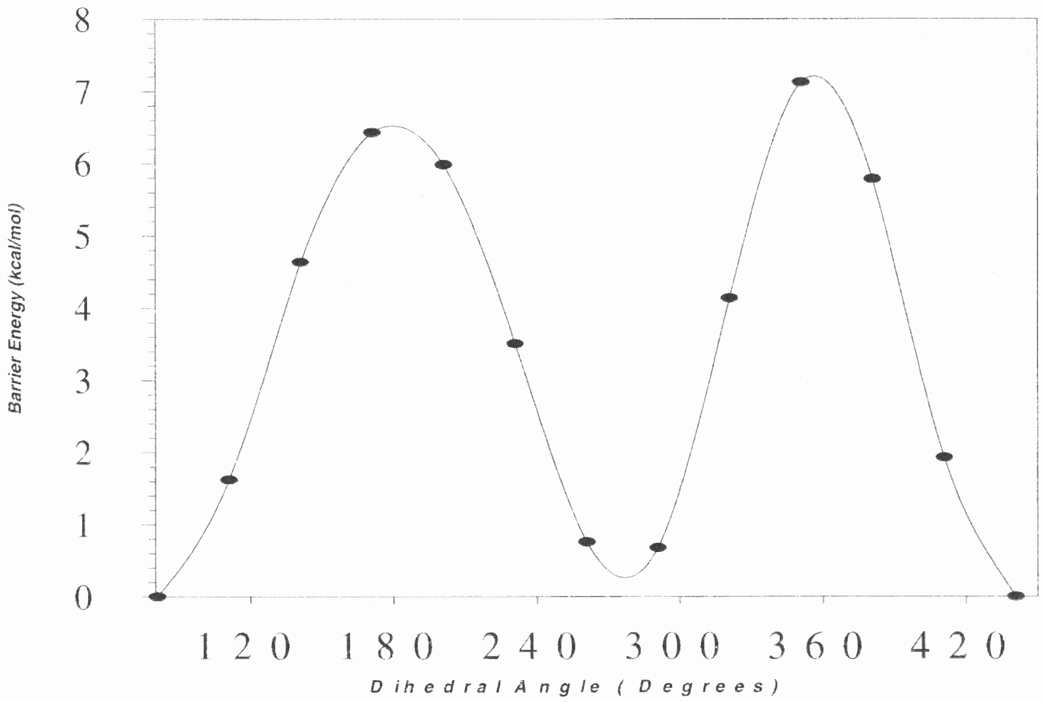


Figure 4.7- Potential energy profile for the $^{\cdot}CH_2S$(S—OC) rotor in $^{\cdot}CH_2SSOCH_3$ molecule

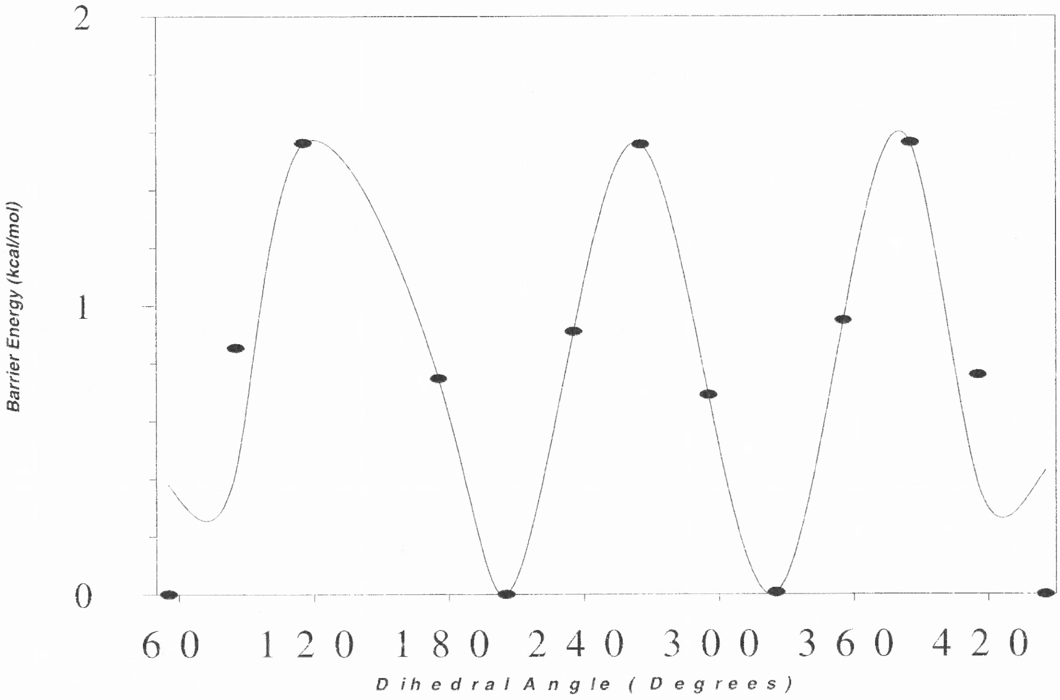


Figure 4.8 Potential energy profile for the ˙CH2-SSO—C rotor in ˙CH_2SSOCH_3 molecule

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 CH_3SSOCH_3 and ˙CH_2SSOCH_3 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°298 and Cp°(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 ($S^0_{(298)}$) and Cp(T) and Heat Capacity

		Cp°(T) (cal mol^{-1} K^{-1})						
Species	S°298 cal mol^{-1} K^{-1}	300K	400K	500K	600K	800K	1000K	1500K
CH_3SSOCH_3	78.80	21.93	26.30	30.19	33.51	38.74	42.66	48.83
**I.R Contribution*								
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
$\bullet CH_2SSOCH_3$	75.49	18.98	22.69	25.84	28.46	32.55	35.61	40.51
I.R Contribution								
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*°298 and *Cp*°(*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 CH_3SSOCH_3 and $\bullet CH_2SSOCH_3$ are -34.33 (+/-0.2) kcal mol^{-1} and 11.44 (+/-0.2) kcal mol^{-1} respectively. The C—H bond energy of CH_3SSOCH_3 is 97.62 kcal mol^{-1}. In the studies undertaken below it has been observed that one of the radicals of CH_3SSOCH_3, namely CH3SSOC·H2 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, $CH_3SS(=O)H$, $^\bullet CH_2SSOH$ and $CH_3SS^\bullet{=}O$

	S°298 (cal mol^{-1} K^{-1})						
Species	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.R Contribution*							
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
$CH_3SS(=O)H$	83.74	109.39	117.28	128.03	143.96	155.60	164.74
**I.R Contribution*							
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
$\bullet CH_2SSOH$	85.64	109.52	116.41	125.70	139.38	149.35	157.18
I.R Contribution							
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
$CH_3SS\bullet{=}O$	78.91	99.75	106.12	114.80	127.67	137.07	144.47
I.R Contribution							
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^o) Data for HSSOH, HSS(=O)H, $^{\bullet}$SSOH and HSS$^{\bullet}$=O

	$S^\circ 298$ (cal mol^{-1} k^{-1})						
Species	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.R Contribution*							
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.R Contribution*							
None	--	--	--	--	--	--	--
Total	101.21	106.30	110.51	114.11	117.24	120.01	122.50
$^{\bullet}$SSOH	94.68	98.47	101.62	104.30	106.64	108.71	110.57
I.R Contribution							
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$^{\bullet}$=O	95.89	99.76	102.95	105.66	108.02	110.11	111.98
I.R Contribution							
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^o) Data for CH_3SSOCH_3 and $^{\bullet}CH_2SSO\ CH_3$

	S^o298 (cal mol^{-1} k^{-1}						
Species	2000 K	2500 K	3000 K	3500 K	4000 K	4500 K	5000 K
CH_3SSOCH_3	150.51	162.32	172.24	180.75	188.20	194.82	200.77
**I.R Contribution*							
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
$\bullet CH_2SSO\ CH_3$	135.81	145.60	153.81	160.86	167.02	172.50	177.42
**I.R Contribution*							
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 CH_3SSOH, $CH_3SS(=O)H$, $^{\bullet}CH_2SSOH$ and $CH_3SS^{\bullet}{=}O$

	Cp°(T) (cal mol^{-1} K^{-1})					
Species	1200 K	1500 K	2000 K	3000 K	4000 K	5000 K
CH_3SSOH	33.91	35.89	37.95	39.84	40.62	41.00
**I.R Contribution*						
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
$CH_3SS(=O)H$	34.32	36.34	38.34	40.08	40.77	41.10
**I.R Contribution*						
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
$^{\bullet}CH_2SSOH$	30.21	31.55	32.99	34.37	34.94	35.23
I.R Contribution						
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
$CH_3SS^{\bullet}{=}O$	27.71	29.33	0.95	32.39	32.97	33.25
I.R Contribution						
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, $^{\bullet}$SSOH and HSS$^{\bullet}$=O

	Cp°(T) (cal mol^{-1} K^{-1}						
Species	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.R Contribution*							
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.R Contribution*							
None	--	--	--	--	--	---	--
Total	22.57	22.99	23.24	23.39	23.49	23.56	23.62
$^{\bullet}$SSOH	16.83	17.15	17.34	17.47	17.56	17.62	17.67
I.R Contribution							
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$^{\bullet}$=O	17.21	17.43	17.56	17.64	17.70	17.73	17.76
I.R Contribution							
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 $CH_3SSO\ CH_3$ and $^{\bullet}CH_2SSOH$

				Cp°(T) (cal mol^{-1} K^{-1})			
Species	2000 K	2500 K	3000 K	3500 K	4000 K	4500 K	5000 K
$CH_3SSO\ CH_3$	52.04	53.82	54.89	55.57	56.03	56.35	56.59
**I.R Contribution*							
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
$^{\bullet}CH_2SSOH$	43.11	44.56	45.44	46.00	46.37	46.64	46.83
**I.R Contribution*							
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 CH_3SSOH

```
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 $CH_3SS(=O)H$

```
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*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
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 •CH_2SSOH

```
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 $CH_3SS^{\bullet}=O$

```
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,
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
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 C8 Input file for HSS$^{\bullet}$=O

```
NAME (name of molecule)
hssoR

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,
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
65.36502 427.18318 482.59420

SYMMETRY
1

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
6
 134.7122              279.4806               436.8018
 779.1475              1054.7745              2657.6253
```

Appendix C9 Input file for CH_3SSOCH_3

```
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 $^{\bullet}CH_2SSO\ CH_3$

```
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 CH$_3$SSOH

```
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*COS(nx)+C*SIN(nx)   b3lyp/6-31G(d,p)
0  0  1
1
300
5
0.5740
0.0100                         -6.9454e-3
-0.0346                        0.0757
0.5484                         0.0403
0.0284                         0.0877
-0.0202                        -2.6755e-3

8
298. 500.
1200. 1500. 2000.
3000. 4000. 5000.
```

Appendix D2 Input file for C-S rotor in $CH_3SS^{\cdot}=O$

```
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*COS(nx)+C*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 $CH_3SS^{\bullet}{=}O$

```
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*COS(nx)+C*SIN(nx)   b3lyp/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 $^{\cdot}CH_2SSOH$

```
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*COS(nx)+C*SIN(nx)  b3lyp/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 $CH_3SS(=O)H$

```
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*COS(nx)+C*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

```
irl-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$^{\cdot}$=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*COS(nx)+C*SIN(nx)  b3lyp/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 CH_3SSOCH_3

```
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 CH_3SSOCH_3

```
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 $^{\cdot}CH_2SSOCH_3$

```
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*COS(nx)+C*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 $^{\cdot}CH_2SSOCH_3$

```
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*COS(nx)+C*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 CH_3SSOH, $CH_3SS(=O)H$, $CH_3SS^{\cdot}=O$ and $^{\cdot}CH_2SSOH$

CH_3SSOH

```
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
 H,7,r87,6,a876,2,d8762,0
      Variables:
 r21=1.8383301
 r31=1.0906966
 r41=1.09336966
 r51=1.0903591
 r62=2.05589967
 r76=1.69654726
 r87=0.97048773
 a312=110.55946989
 a412=106.32526784
 a512=110.10870109
 a621=103.87868449
 a762=106.4202714
 a876=106.61129892
 d4123=118.99948802
 d5123=-122.42227841
 d6213=59.38385256
 d7621=81.93370196
 d8762=84.948916
```

$CH_3SS(=O)H$

```
C
 S,1,B1
 H,1,B2,2,A1
 H,1,B3,2,A2,3,D1,0
 H,1,B4,2,A3,4,D2,0
 S,2,B5,1,A4,4,D3,0
 O,6,B6,2,A5,1,D4,0
 H,6,B7,2,A6,1,D5,0
      Variables:
 B1=1.83044132
 B2=1.09465741
 B3=1.09116124
 B4=1.09171001
 B5=2.18349949
 B6=1.50357617
 B7=1.387087
 A1=108.10860497
 A2=107.29600786
 A3=111.44646049
 A4=97.26680918
 A5=110.12882626
 A6=91.9877312
 D1=117.47958913
 D2=120.6304162
 D3=150.82002628
 D4=-39.1412079
 D5=69.27499323
```

$CH_3SS^{\cdot}=O$

```
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
      Variables:
 r21=1.83078171
 r31=1.09084113
 r41=1.09075295
 r51=1.09311219
 r62=2.15321433
 r76=1.51683246
 a312=110.67512011
 a412=107.04971634
 a512=108.66665978
 a621=99.13115752
 a762=109.23119195
 d4123=120.33493489
 d5123=-121.44306616
 d6213=91.79484477
 d7621=24.46236303
```

$^{\cdot}CH_2SSOH$

```
C
 S,1,r21
 H,1,r31,2,a312
H,1,r41,2,a412,3,d412
S,2,r52,1,a521,3,d521
O,5,r65,2,a652,1,d652
H,6,r76,5,a765,1,d765
      Variables:
 r21=1.7278414
 r31=1.08287113
 r41=1.0833634
 r52=2.08774626
 r65=1.69295234
 r76=0.97078554
 a312=120.93898566
 a412=117.55819478
 a521=105.60482961
 a652=106.97590872
 a765=106.71281175
 d4123=-179.24478202
 d5213=29.72892473
 d6521=80.45428996
 d7651=118.45973984
```

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

HSSOH

```
S
 H,1,r21
 S,1,r31,2,a312
O,3,r43,1,a431,2,d4312,0
H,4,r54,3,a543,1,d5431,0
      Variables:
 r21=1.3550719
 r31=2.0747551
 r43=1.68787042
 r54=0.9707062
 a312=99.8904746
 a431=106.15843093
 a543=106.89533992
 d4312=-84.0067879
 d5431=-85.50705504
```

HSS(=O)H

```
S
 H,1,B1
 S,1,B2,2,A1
H,3,B3,1,A2,2,D1,0
O,3,B4,1,A3,2,D2,0
      Variables:
 B1=1.34977143
 B2=2.19967835
 B3=1.38791536
 B4=1.49277934
 A1=93.70459039
 A2=85.33722116
 A3=114.04808667
 D1=-164.28121575
 D2=87.25604374
```

HSS·=O

```
S
 H,1,r21
 S,1,r31,2,a312
O,3,r43,2,a432,1,d4321,0
      Variables:
 r21=1.35178851
 r31=2.14866759
 r43=1.51487236
 a312=95.99982656
 a432=95.81726132
 d4321=-121.80423762
```

·SSOH

```
S
 S,1,r21
 O,2,r32,1,a321
H,3,r43,2,a432,1,d4321
      Variables:
 r21=1.95529458
 r32=1.6869813
 r43=0.9729604
 a321=110.12714298
 a432=108.54945343
 d4321=-50.53127601
```

Appendix E3 Optimized Z-matrix from B3LYP/6-31G (d, p) for CH_3SSOCH_3, and $^{\cdot}CH_2SSOCH_3$

CH_3SSOCH_3

```
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
```

$^{\cdot}CH_2SSOCH_3$

```
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

	Energy in Hartrees		
Species	**B3LYP/6-31G (d, p)**	**B3LYP/6-311++G (3df, 2p)**	**CBS-QB3**
CH_3SSOH	-912.0404383	-912.162441	-911.03635
$CH_3SS(=O)H$	-912.0022002	-912.1361146	-911.01168
$CH_3SS^{\cdot}=O$	-911.4252196	-911.5505085	-910.425023
$^{\cdot}CH_2SSOH$	-911.3877641	-911.5131084	-910.383028
HSSOH	-872.7510126	-872.8633697	-871.810461
HSS(=O)H	-872.7144868	-872.8404051	-871.788268
$HSS^{\cdot}=O$	-872.1359678	-872.2525627	-871.200048
$^{\cdot}SSOH$	-872.1479125	-872.2608154	-871.207396
CH_3SSOCH_3	-951.3179301	-951.4476475	-950.247667
$^{\cdot}CH_2SSOCH_3$	-950.6644836	-950.7973246	-949.594152

Appendix F2 List of Energies for the Reference Species

	Energy in Hartrees		
Species	**B3LYP/6-31G (d, p)**	**B3LYP/6-311++G (3df, 2p)**	**CBS-QB3**
C_2H_6	-79.76083556	-79.78359386	-79.626119
CH_4	-40.476056	-40.4887964	-40.406185
HSH	-399.3730069	-399.4103369	-398.931111
CH_3SH	-438.6557805	-438.7025704	-438.148253
CH_3OH	-115.6693117	-115.7182667	-115.535673
CH_3SSH	-836.8364619	-836.9194279	-835.902689
CH_3SCH_3	-477.9419497	-477.9982167	-477.370613
CH_3SOH	-513.8381582	-513.9237902	-513.269424
C_2H_5OH	-154.9676045	-155.0263811	-154.76488
HSSH	-797.5482012	-797.6219347	-796.67016
$CH_3S(=O)H$	-513.8105466	-513.9098372	-513.256135
C_2H_5SH	-477.943607	-478.000682	-477.373385
HSOH	-474.5451671	-474.6209277	-474.040578
CH_3SSCH_3	-876.1240896	-876.2172421	-875.118794
$CH_3SC_2H_5$	-517.2295132	-517.2963094	-516.595738
$CH_3O^\cdot$	-115.0147854	-115.059384	-114.870514
$C_2H_5O^\cdot$	-154.309699	-154.3638915	-154.100554
$CH_3S^\cdot{=}O$	-513.2329902	-513.3224486	-512.667759
$CH_3S^\cdot$	-438.0249479	-438.0686994	-437.512066
$^\cdot CH_2SH$	-438.0044424	-438.0551627	-437.498456
$CH_3C^\cdot HSH$	-477.2968692	-477.3568315	-476.725965
$HS^\cdot{=}O$	-473.9336888	-474.0023138	-473.432549
$^\cdot SH$	-398.7340004	-398.7340004	-398.287356
$^\cdot CH_2SCH_3$	-477.2925245	-477.3532173	-476.722804

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