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## ABSTRACT

# THERMOCHEMICAL PROPERTIES OF SMALL OXYGENATED SULFUR HYDROCARBONS AND KINETICS - REACTION PATHWAYS OF METHYLTHIOMETHYL RADICAL WITH OXYGEN

by  
Fei Jin

The thermochemical properties on  $\text{CH}_3\text{SCH}_2\text{OOH}$  and the corresponding two radicals resulting from loss of H atom:  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  are important to understand the stability, reaction paths and kinetics of reactions of dimethyl sulfide and other sulfur hydrocarbons (sulfides) in the atmosphere and combustion processes. Thermochemical properties for species and transition states in the methylthiomethyl radical ( $\text{CH}_3\text{SC}\cdot\text{H}_2$ ) +  $\text{O}_2$  reaction system are analyzed to evaluate reaction paths and kinetics under these conditions. Isodesmic working reaction are employed to determine the enthalpies of formation ( $\Delta H_f^\circ_{298}$ ) using density functional (B3LYP/6-311G(d,p)) and complete basis set extrapolation (CBS-QB3) computational methods. Entropy ( $S^\circ_{298}$ ) and heat capacities  $C_p(T)$  ( $300 \leq T/\text{K} \leq 1500$ ) are determined using geometric parameters and vibration frequencies obtained at B3LYP/6-311G(d,p) level of calculation. Quantum Rice-Ramsperger-Kassel(QRRK) analysis is used to calculate energy- dependent rate constants,  $k(E)$  and master equation is used to account for collisional stabilization of adduct and isomer. The methylthiomethyl radical adds to oxygen to form a methylperoxy radical with a 37.82 kcal/mol well depth. The peroxy radical can undergo dissociation back to reactants, isomerize via hydrogen shift (TS1,  $E_a=17.06\text{kcal/mol}$ ) to form a hydroperoxide methyl radical  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$ , decompose via hydrogen transfer (TS2,

$E_a=37.79\text{kcal/mol}$ ) to form  $\text{CH}_3\text{SC}(=\text{O})\text{H}$  plus OH radical, or the peroxy radical can also attack the sulfur atom via TS3 ( $E_a=32.92\text{kcal/mol}$ ) to form  $\text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$ . The  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  isomer can decompose via TS4 ( $E_a=24.09\text{kcal/mol}$ ) to form  $\text{CH}_2\text{O}+\text{CH}_2\text{S}+\text{OH}$ , or through a four-member ring transition state (TS5,  $E_a=30.77\text{kcal/mol}$ ) to form 1,3-Oxathietane + OH.

Structures and thermochemical properties on Sulfenic Acids (RSOH R =  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ ,  $\text{CH}_2=\text{CH}$ ;) and their radicals are determined by CBS-QB3 calculation. Molecular structures and vibration frequencies are calculated at B3LYP/6-311G(d,p) levels.  $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$  and  $C_p(\text{T})$  for the concerned species are calculated in this study. Enthalpies of formation are determined using the  $\Delta H^\circ_{\text{rxn}(298)}$  and known enthalpies in each of different working reactions. Contributions to entropy and heat capacity from internal rotation are also determined.

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HYDROCARBONS  
AND  
KINETICS - REACTION PATHWAYS OF METHYLTHIOMETHYL RADICAL  
WITH OXYGEN**

**by  
Fei Jin**

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**APPROVAL PAGE**

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**This thesis is dedicated to my beloved husband and my parents.**

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## CHAPTER 1

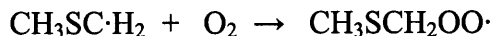
### THERMODYNAMIC AND KINETIC ANALYSIS ON METHYLTHIOMETHYL RADICAL WITH OXYGEN

#### 1.1 Introduction

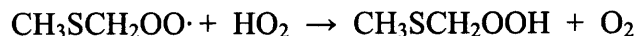
Dimethyl sulfide (DMS) has been recognized as the main natural source of sulfur in the atmosphere [1]. It emitted into the atmosphere over the global oceans has a range of effects upon atmospheric composition (mediated through various oxidation products) that may be significant with regard to issues as important as climate regulation. The roles played by DMS oxidation products are diverse and complex. Components of the chemistry are, in many instances, not well understood.

At present, the main step of the DMS oxidation in the atmosphere is the reaction with OH [2] radical during daylight and the reactions with NO<sub>3</sub> [3] radical and Cl [4] radical, these reactions will lead to the formation of the CH<sub>3</sub>SC·H<sub>2</sub> radical.

The CH<sub>3</sub>SCH<sub>2</sub>OO peroxy radical (methyl-thiol-methyl peroxy radical) is then (immediately) formed through reaction with oxygen in the atmosphere. This is an important intermediate in the atmospheric degradation of dimethyl sulfide [5,6]. The CH<sub>3</sub>SCH<sub>2</sub>OO· peroxy radical is produced through the association the CH<sub>3</sub>SCH<sub>2</sub> radical with O<sub>2</sub>:



It is believed that the reaction of the CH<sub>3</sub>SCH<sub>2</sub>OO· with the HO<sub>2</sub> radical will lead to the following products:



Wallington et al suggested this reaction would be the dominant one for reaction with HO<sub>2</sub> and it could play a significant role in the atmospheric degradation of DMS. The rate constant was estimated as  $k = 5 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , which will lead to an atmospheric lifetime of 3 minutes for the CH<sub>3</sub>SCH<sub>2</sub>OO· radical.

There are no studies on the overall kinetics of the complex process involved in the di-methyl sulfide radical reaction with O<sub>2</sub> and there are not studies of the kinetic parameters to the varied reaction paths for either the chemical activated or the dissociation of the thermally stabilized dimethylsulfide peroxy radical.

The thermochemical properties of the species in the reaction of CH<sub>3</sub>SC·H<sub>2</sub> + O<sub>2</sub> have been studied by several research groups. Stella et al. have reported thermochemical data for CH<sub>3</sub>SCH<sub>2</sub>OOH ( $\Delta H_f^\circ_{298} = -28.4 \text{kcal/mol}$ ) and CH<sub>3</sub>SCH<sub>2</sub>OO· ( $\Delta H_f^\circ_{298} = 6.51 \text{kcal/mol}$ ) at the CCSD(T)/cc-Pvtz//MP2/6-31G(d) level.

McKee have calculated the heat formation of the CH<sub>3</sub>SCH<sub>2</sub>OO· and CH<sub>3</sub>SCH<sub>2</sub>O· radicals at the QCISD(T)/6-31+G(2df,p)//MP2/6-31G+d level of theory, using isodesmic reactions. The values were 5.9 kcal/mol and 7.4 kcal/mol, respectively.

In this chapter, reaction pathways of the addition of O<sub>2</sub> to CH<sub>3</sub>SC·H<sub>2</sub> radical are analyzed. CBS-QB3 and density functional methods are utilized to estimate thermodynamic properties ( $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$  and  $C_p(T)$ ) for reactant CH<sub>3</sub>SC·H<sub>2</sub>, intermediate radicals CH<sub>3</sub>SCH<sub>2</sub>OO·, C·H<sub>2</sub>SCH<sub>2</sub>OOH and transition states:

TS1:  $\overline{\text{CH}_3\text{SCH}_2\text{OO}}$  Intramolecular hydrogen shift to form a hydroperoxy radical.

TS2:  $\overline{\text{CH}_3\text{SCH}_2\text{OO}}$  Intramolecular hydrogen shift to form CH<sub>3</sub>S·CHOOH radical, and CH<sub>3</sub>S·CHOOH rapidly dissociates CH<sub>3</sub>SC(=O)H + OH.

TS3:  $\overline{\text{CH}_3\text{SCH}_2\text{OO}}$  The peroxy radical attack the sulfur atom form  $\text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$ .

TS4:  $\text{CH}_2\text{S}-\text{CH}_2\text{O}-\text{OH}$   $\beta,\gamma$ -scission reaction to form a thioformaldehyde plus a formaldehyde and OH.

TS5:  $\overline{\text{CH}_2\text{SCH}_2\text{O}}-\text{OH}$  1,3-Oxathietane + OH.

Isodesmic working reactions are applied to evaluate enthalpies of formation. Contributions to entropy and heat capacities from internal rotation are estimated using direct integration over energy level of the intermolecular rotation potential energy curve, with B3LYP/6-311g(d,p) level of calculation for rotation barrier. Activation energies for the transition states are determined and the kinetic analysis is detailed on the base of the thermodynamic properties.

Quantum Rice-Ramsperger-Kassel (QRRK) analysis [7] is used to calculate the energy dependent rate constant  $k(E)$ , and master equation analysis is applied to account for collisional stabilization in the  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$  adduct and isomers. The thermochemical and kinetic data at relevant pressures and temperatures should be useful to both atmospheric and combustion models.

## 1.2 Calculation Method

All the calculations were carried out using Gaussian 98 program [8]. The geometry optimization, harmonic vibration frequencies are computed with the B3LYP/6-311G(d,p) level of theory transition state geometries are identified by the existence of only one imaginary frequency.

To improve the accuracy of the calculated values on relative energies we used one the Complete Basis Set series, namely CBS-QB3 [9]. This approach employs B3LYP

geometries as the basis for a series of single point calculations and empirical corrections.

The single point calculations include:

- A large basis set Hartree –Fock calculation at MP4SDQ/CBSB4 level.
- A complete basis set extrapolation at MP2/CBSB3 level.
- Higher level correlation is included at CCSD(T)/6-31+G(d') level.

### 1.2.1 Enthalpies of Formation ( $\Delta H_f^\circ$ )

Enthalpies of formation ( $\Delta H_f^\circ$ ) for reactant, intermediate radicals and their parent molecule  $\text{CH}_3\text{SCH}_2\text{OOH}$  which are necessary to calculate intermediate radicals are estimated using total energies obtained by density functional (B3LYP/6-311G(d,p)) and CBS-QB3 calculations combined with the use of isodesmic working reactions. Total energies are corrected by zero-point vibrational energies (ZPVE), which are scaled by 0.9806 [10] for the B3LYP/6-311G(d,p) level. ZPVE's calculated by CBS-QB3 level of theory are scaled by 0.99[9].

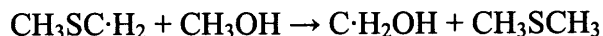
$$\Delta H(T) = H_{\text{trans}}(T) + H_{\text{rot}}(T) + \Delta H_{\text{vib}}(T) + RT$$

$$H_{\text{trans}}(T) = 3/2 RT ; \quad H_{\text{rot}}(T) = 3/2 RT$$

$$\Delta H_{\text{vib}}(T) = Nh \sum ( \nu_i / (\exp(h\nu_i / k_b T) - 1) )$$

where  $N$  is Avogadro constant,  $h$  is Planck constant, and  $k_b$  is Boltzmann constant.

Isodesmic reactions are hypothetical reactions where the number of electron pairs and the bonds of the same type are conserved on both sides of the equation. The working reaction is utilized in way that leads cancellations [11]. For an example, one working reaction for estimation of  $\text{CH}_3\text{SC}\cdot\text{H}_2$  is



All four compounds in this reaction are estimated using density functional and CBS-QB3 calculations. Since  $\Delta H_f^\circ_{298}$  of three compounds (except  $\text{CH}_3\text{SC}\cdot\text{H}_2$ ) have been experimentally or theoretically calculated, the unknown  $\Delta H_f^\circ_{298}$  for  $\text{CH}_3\text{SC}\cdot\text{H}_2$  is obtained.

Enthalpy values for the transition state saddle points are estimated by evaluation of  $\Delta H_f^\circ_{298}$  of the stable radical adduct plus the difference of the total energies with ZPVE and thermal correction between the reactant or product radical species and the transition state.

### 1.2.2 Entropy ( $S^\circ_{298}$ ) and Heat Capacities ( $C_p(T)$ , $300 \leq T/K \leq 1500$ )

Entropies and heat capacities at temperature range from 300K to 1500K were calculated using the rigid-rotor-harmonic-oscillator approximation based on scaled vibrational frequencies and moments of inertia of the optimized BLYP/6-311G(d,p) structures. Contribution to entropy and heat capacity from internal rotation is determined using Pitzer et al's treatment [12] based on rotational barrier height and corresponding moments of inertia for the rotors. SMCPS program was used.

### 1.2.3 High-Pressure Limit $A$ Factors( $A$ ) and Rate Constant ( $k_\infty$ )

Thermochemical properties entropy and heat capacity of transition states are calculated by B3LYP/6-311g(d,p) density functional method. Enthalpy values of the transition states are calculated with this B3LYP/6-311g(d,p) method and with CBS-QB3method.

High-pressure limit rate constants,  $k_\infty$ , are calculated using the  $E_a$  described below and pre-exponential values ( $A$  factors). This pre-exponential factor are from entropy differences between reactant and transition state  $\Delta S^\ddagger$  over the temperature range from

200K to 2000K are used to determine the pre-exponential factor  $A$ , via classical, canonical TST for a unimolecular reaction

$$A = (\kappa_b T / h_p) \exp(\Delta S^\ddagger / R)$$

where  $h_p$  is the Planck constant and  $\kappa_b$  is Boltzmann constant,  $R=1.987\text{cal}/(\text{mol K})$ .

These  $k$  infinity values are fit by three parameters,  $A$ ,  $n$ , and  $E_a$  over the temperature range from 200K to 2000K, expressed by:

$$k_\infty = A(T)^n \exp(-E_a/RT)$$

Activation energies of reactions are calculated as follows:

$$E_a = [\Delta H_f^\circ_{298, \text{TS}} - \Delta H_f^\circ_{298, \text{reactant}}]$$

#### 1.2.4 Quantum Rice-Ramsperger-Kassel Analysis with Master Equation

Quantum Rice-Ramsperger-Kassel (QRRK) analysis is used to calculate  $k(E)$  with a master equation analysis [13] for falloff in order to obtain rate constants as a function of temperature and pressure. Reduced sets of three vibrational frequencies and their degeneracy plus energy levels of one external rotor are used to yield the ratio of density of states to partition the coefficient,  $\rho(E)/Q$  for each adduct (isomer in the chemical activation or dissociation reaction system). Each set of vibrational frequencies and respective degeneracies is computed from fitting heat capacity data, as described by Ritter (CPFIT computer code)[14].

## 1.3 Results and Discussion

### 1.3.1 Geometries and Vibrational Frequencies

Figure 1.1 shows the optimized geometric structures of  $\text{CH}_3\text{SCH}_2\text{OOH}$ ,  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$ ,  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  and transition states, calculated at B3LYP/6-311g(d,p) level. In the stable molecule and two radicals, the oxygen bonded to the carbon in three structures is almost perpendicular to the plane of the C-S-C. The results with data (in the parenthesis) reported previously by Stella et al, which is at the UMP2/6-31G(d) calculation level, are compared with this work. TS1 for isomerization of  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  to  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  is a six-member ring. The O-H bondlength is 1.17Å and the C-H bondlength is 1.40 Å, both slightly longer than the stable O-H bondlength (0.96Å), and the stable C-H bondlength (1.08Å). TS2 for intramolecular hydrogen shift from  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  to  $\text{CH}_3\text{SC}\cdot\text{HOOH}$  has an O-H bondlength of 1.31Å and the C-H bondlength of 1.30 Å, both slightly longer than the stable O-H bondlength, 0.96 Å, and the C-H bondlength 1.08 Å. The TS3 shows a C-S cleaving bond of 2.00 Å and S-O forming bond of 1.90 Å. TS4 for the formation of the  $\text{CH}_2\text{S}+\text{CH}_2\text{O}+\text{OH}$  has S-C lengthening bond 2.04 Å and C-O lengthening bond 1.81 Å. TS5 for 1,3-Oxathietane + OH formation has a four-member ring structure. The dissociating O-O bond is 1.71 Å and the forming C-O bond is 2.00 Å.

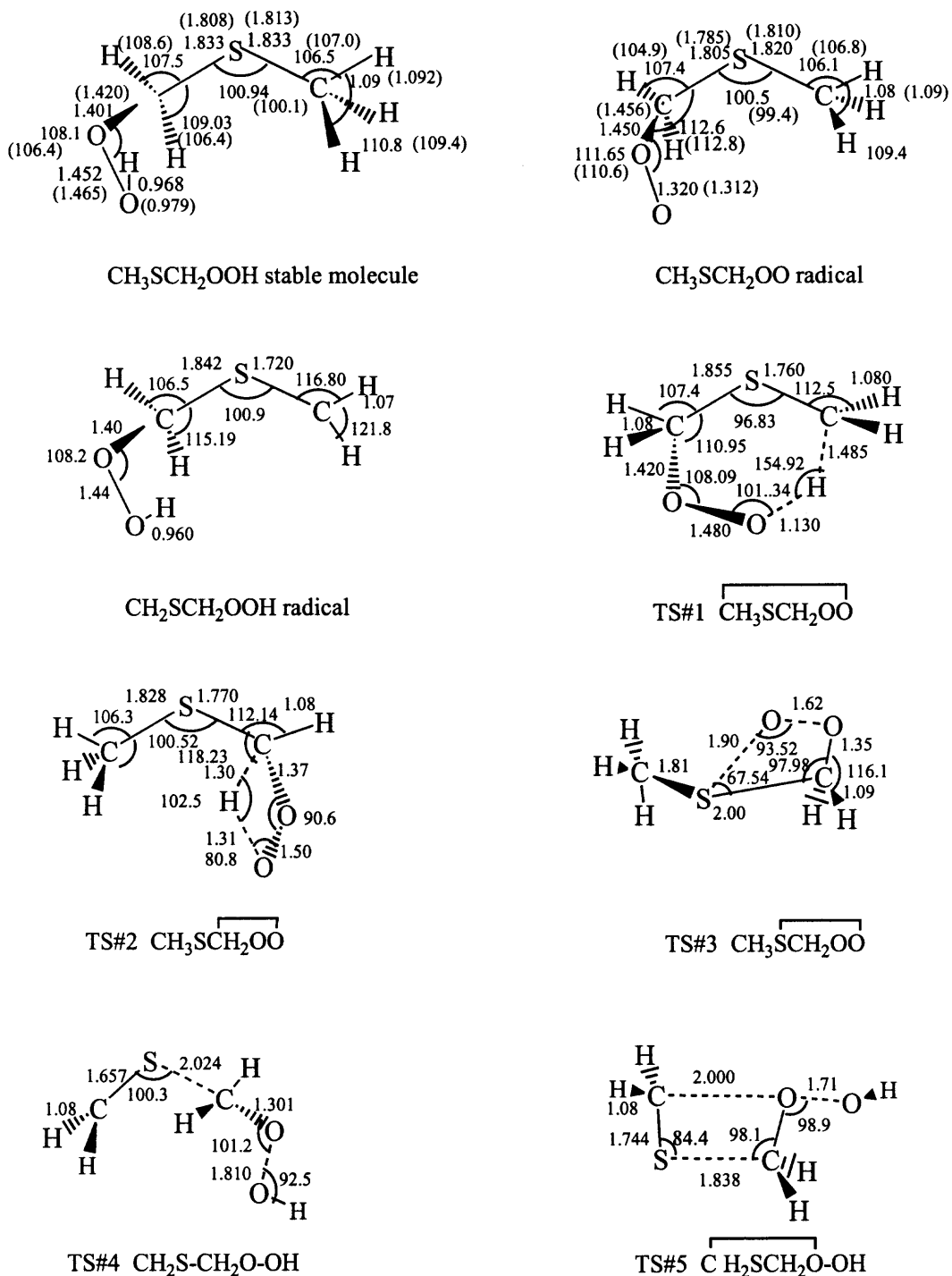
Harmonic vibrational frequencies are calculated for the reactant, intermediates and the transition states at the B3LYP/6-311g(d,p) level of theory on the basis of optimized geometries at the same level of theory. The vibrational frequencies and moments of inertia are given in Table 1.1



**Table 1.1** Vibration Frequencies and Moments of Inertia

	Moments of inertia (amu Bohr <sup>2</sup> )	Frequencies (cm <sup>-1</sup> )
CH <sub>3</sub> S·H <sub>2</sub>	87.80916 226.60564 301.98115	162, 216, 293, 396, 691, 829, 9023, 971, 1035, 1357, 1408, 1467, 1482, 3043, 3125, 3140, 3146, 3273,
CH <sub>3</sub> SCH <sub>2</sub> OOH	275.94881 683.42678 841.48374	81, 121, 140, 250, 291, 343, 491, 682, 712, 858, 920, 979, 1003, 1042, 1277, 1321, 1363, 1378, 1432, 1466, 1490, 3045, 3047, 3120
CH <sub>3</sub> SCH <sub>2</sub> OO·	202.79126 824.51025 946.42836	79, 113, 159, 252, 351, 514, 681, 728, 829, 920, 982, 1036, 1146, 1277, 1317, 1368, 1430, 1467, 1480, 3048, 3077, 3135, 3143, 3155
C·H <sub>2</sub> SCH <sub>2</sub> OOH	256.86215 650.99354 819.68014	71, 134, 170, 263, 290, 329, 354, 490, 675, 814, 8566, 906, 996, 1035, 1277, 1317, 1377, 1398, 1430, 3055, 3130, 3159, 3291, 3749
$\overline{\text{CH}_3\text{SCH}_2\text{OO}}$ (TS1)	275.03807 515.53592 723.50121	1642i, 183, 358, 376, 445, 510, 610, 662, 772, 899, 954, 1011, 1019, 1027, 1196, 1261, 1300, 1428, 1444, 1565, 3063, 3077, 3149, 3186
$\overline{\text{CH}_3\text{SCH}_2\text{OO}}$ (TS2)	244.36665 668.30811 802.73542	1725i, 57, 103, 148, 248, 421, 589, 684, 800, 807, 890, 980, 995, 1091, 1118, 1296, 1359, 1460, 1481, 1976, 3061, 3083, 3150, 3167
$\overline{\text{CH}_3\text{SCH}_2\text{OO}}$ (TS3)	272.93631 538.28462 555.73710	1004i, 88, 168, 198, 281, 362, 460, 649, 693, 879, 950, 994, 1090, 1178, 1237, 1341, 1460.12, 1470, 1496, 3003, 3043, 3086, 3134, 3154
C·H <sub>2</sub> S-CH <sub>2</sub> O-OH (TS4)	292.67278 636.78087 835.91944	828i, 96, 130, 179, 222, 241, 356, 446, 516, 794, 882, 902, 947, 1000, 1109, 1189, 1293, 1433, 1442, 2962, 3036, 3121, 3250, 3802
$\overline{\text{CH}_2\text{SCH}_2\text{O-OH}}$ (TS5)	186.04990 750.05334 895.75778	800i, 104, 166, 208, 246, 352, 475, 534, 715, 784, 849, 939, 967, 991, 1074, 1167, 1284, 1437, 1511, 3051, 3126, 3131, 3249, 3794

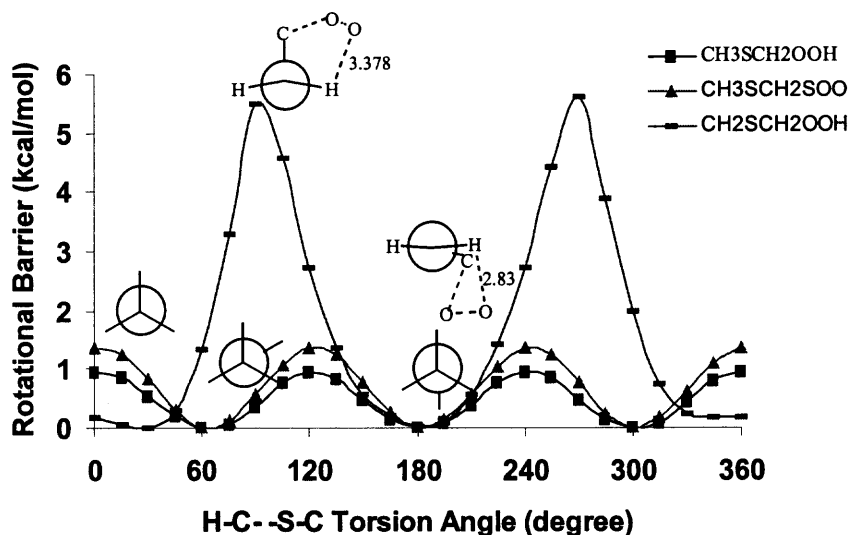
Radical site is identified by (•),  $\overline{\quad}$  \ denotes cyclic component of molecule or transition state structure.



**Figure 1.1** Structures and geometrical parameters for all species studied at B3LYP/6-311G(d,p) Distance is present in Å and angles in degrees. The values calculated by Stella, at the UMP2/6-31G(d) level of theory are in the parenthesis.

### 1.3.2 Rotational Barrier

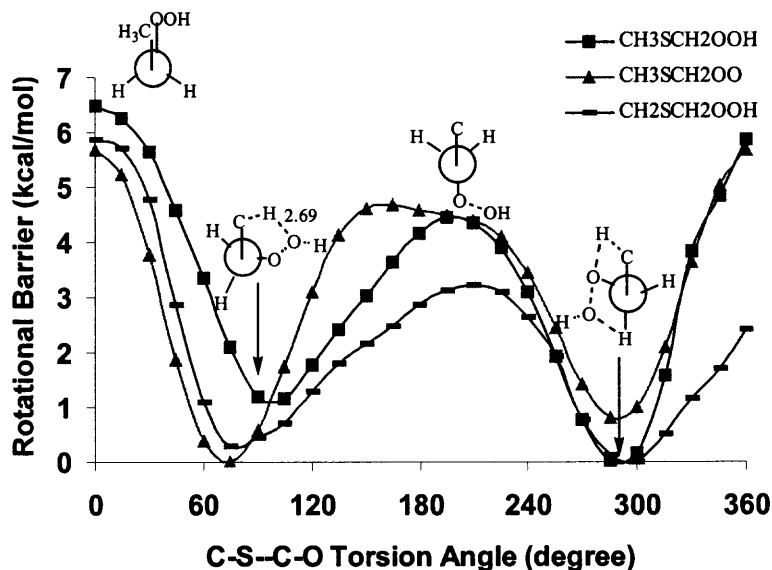
Potential barrier for internal rotations of the reactant peroxy radical ( $\text{CH}_3\text{SCH}_2\text{OO}\cdot$ ), hydroperoxide alkyl radical ( $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OO}$ ) and their parent molecule  $\text{CH}_3\text{SCH}_2\text{OOH}$  are calculated at the B3LYP/6-311g(d,p) level. Potential energy as function of dihedral angle is determined by varying the torsional angle from  $0^\circ$  to  $360^\circ$  at  $15^\circ$  intervals and allowing the remaining structure parameters to be optimized at B3LYP/6-311g(d,p) level. The barrier of a given rotation is then calculated as the difference between the highest point on the potential energy surface and the corresponding most stable conformer. Potential energy vs. torsion angle diagrams of internal rotations about H-C--S-C; C-S--C-O; S-C--O-O and C-O--O-H are shown for three species in Figures 1.2, 1.3, 1.4 and 1.5.



**Figure 1.2** Potential barrier for internal rotation about the C—S bond of  $\text{CH}_3\text{SCH}_2\text{OOH}$ ,  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OO}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.

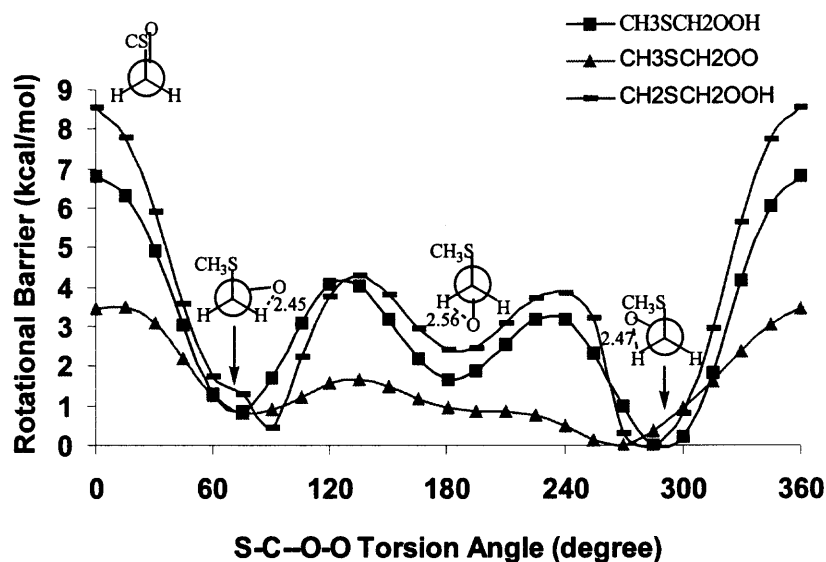
The calculated rotational barriers vs torsional angle about C—S bond of the three target species shown in Figure 1.2 present the three curves. For  $\text{CH}_3\text{—SCH}_2\text{OOH}$ ,  $\text{CH}_3\text{—SCH}_2\text{OO}\cdot$ , they have three minima and three maxima and indicate 3-fold symmetry with

barriers between 0.96 and 0.55 kcal/mol. These two curves represent typical  $\text{CH}_3\text{—S}$  bond rotational potentials, in which the eclipsed structures are corresponding to the maxima and the staggered structures are corresponding to the minima on the potential curve. The  $\text{CH}_2\text{—S}$  torsion potential for  $\text{C}\cdot\text{H}_2\text{—SCH}_2\text{OOH}$  radical show  $A_2$ -fold symmetry. The conformer with dihedral  $\angle\text{H—C—S—C}$  is  $30^\circ$  or  $180^\circ$  is the most stable because of electrostatic repulsions; the  $\text{O}\cdots\text{H}$  interaction [16,17] between H atom in the  $-\text{CH}_2-$  group and the peroxy O atom, with the inter atomic distance of  $2.830 \text{ \AA}$  (dihedral angle is  $180^\circ$ ) and  $2.890 \text{ \AA}$  (dihedral angle is  $30^\circ$ ), which is nearly equal to the van der Waals radii for O and H atom ( $2.70 \text{ \AA}$ ). But when the dihedral angle approaches  $90^\circ$  and  $270^\circ$ , the interatomic distance is  $3.678 \text{ \AA}$  and  $3.222 \text{ \AA}$ , respectively. The structures with the  $2.8 - 2.9 \text{ \AA}$  distances have lower energy by some  $5.5 \text{ kcal/mol}$  due to hydrogen bonding in those conformers.



**Figure 1.3** Potential barrier for internal rotation about the  $\text{S—C}$  bond of  $\text{CH}_3\text{SCH}_2\text{OOH}$ ,  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.

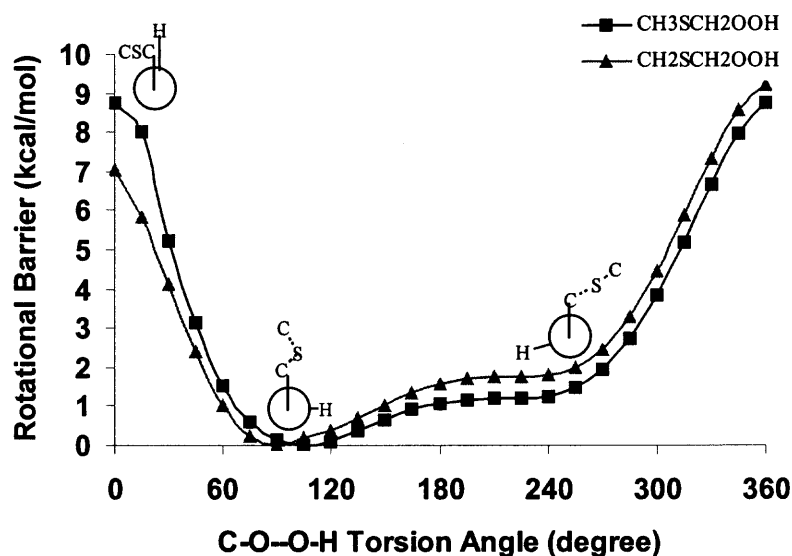
The calculated rotational barriers about the CS—COO bond of CH<sub>3</sub>S—CH<sub>2</sub>OOH, CH<sub>3</sub>S—CH<sub>2</sub>OO· and C·H<sub>2</sub>S—CH<sub>2</sub>OOH are shown in Figure 1.3. The most stable conformer for three species has the dihedral  $\angle$ H-C--S-C $\approx$ 75° or at 300°, which indicates a gauche preference for this set of 4 atoms. Rotation of three species about this CS—COO bond offers the potential barrier 5.58 kcal/mol, 5.10 kcal/mol and 4.54 kcal/mol.



**Figure 1.4** Potential barrier for internal rotation about the C—O bond of CH<sub>3</sub>SCH<sub>2</sub>OOH, CH<sub>3</sub>SCH<sub>2</sub>OO· and C·H<sub>2</sub>SCH<sub>2</sub>OOH. Points are calculated value at the B3LYP/6-311G(d,p) level.

The calculated rotational barriers about the RSC—OO bond of CH<sub>3</sub>SCH<sub>2</sub>—OOH, CH<sub>3</sub>SCH<sub>2</sub>—OO· and C·H<sub>2</sub>SCH<sub>2</sub>—OOH are shown in Figure 1.4. The conformers with the dihedral angle  $\angle$ S-C--O-O ranging from 270° to 290° are the most stable because the electrostatic interactions of the peroxy O atom with the H atom in the —CH<sub>2</sub>— and —CH<sub>3</sub> group. The conformers with dihedral angle 90° and 180° only have the interaction between peroxy O atom with the H atom in the —CH<sub>2</sub>— group. The highest rotation

barriers about the C—O bond of  $\text{CH}_3\text{SCH}_2\text{OOH}$ ,  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  are 5.5, 2.56 and 6.41kcal/mol, respectively.



**Figure 1.5** Potential barrier for internal rotation about the O—O bond of  $\text{CH}_3\text{SCH}_2\text{OOH}$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.

The calculated rotational barriers about the CSCO—OH bond of  $\text{CH}_3\text{SCH}_2\text{O—OH}$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{O—OH}$  are shown in Figure 1.5. The skew conformations are the most stable in the  $\angle\text{C-O-O-H}$  dihedral angle ranging from  $90^\circ$  to  $105^\circ$ . The orthogonal conformation allows for greater delocalization of lone pair electrons on two oxygen atoms than do the coplanar conformations (cis and trans); the nearest interatomic distances between peroxy H atom and the S atom correspond to the most stable conformers.  $\text{CH}_3\text{SCH}_2\text{OOH}$  conformer has the highest barrier of 8.77kcal/mol. In the  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  radical, the repulsion between the peroxy H atom the SC group at the dihedral angle of  $0^\circ$  has the highest energy 9.21kcal/mol.

### 1.3.3 Enthalpies of Formation ( $\Delta H_f^\circ$ 298)

The enthalpies of formation ( $\Delta H_f^\circ$  298) are estimated using total energies and calculated  $\Delta H_{\text{rxn}298}$  for the listed reactions. The total energies are determined at the CBS-QB3 level; scaled ZPVE's and thermal corrections to 298.15K are listed in Table 1.3.

The  $\Delta H_f^\circ$  298 for reactant and intermediates are determined from total energies and isodesmic reactions. All four compounds in each reaction are estimated using density functional and CBS-QB3 calculations. ZPVE's and thermal correction are taken into account. And the enthalpy of reaction ( $\Delta H^\circ_{\text{rxn}}$ ) are obtained. Since  $\Delta H_f^\circ$  298 of other three compounds have been experimentally determined or theoretically calculated, the unknown enthalpies of the target species are calculated.

Enthalpies of formation and their corresponding uncertainties for standard species used in the isodesmic working reactions are obtained from evaluation of literature data. The values are listed in Table 1.2.

**Table 1.2**  $\Delta H_f^\circ$  298 for Species in Working Reactions

Species	$\Delta H_f^\circ$ 298 (kcal/mol)	Species	$\Delta H_f^\circ$ 298 (kcal/mol)
CH <sub>4</sub> [18]	-17.89±0.07	CH <sub>3</sub> CH <sub>2</sub> OOH [23]	-39.7±0.3
C <sub>2</sub> H <sub>6</sub> [18]	-20.04± 0.12	CH <sub>3</sub> OOH [14]	-31.8±0.94
C <sub>3</sub> H <sub>8</sub> [19]	-25.02±0.12	CH <sub>3</sub> OO· [15]	2.15±1.22
CH <sub>3</sub> SCH <sub>3</sub> [20]	-8.96±0.48	CH <sub>3</sub> CH <sub>2</sub> OO· [25]	-6.5±2.4
CH <sub>3</sub> SCH <sub>2</sub> CH <sub>3</sub> [21]	-14.42±0.27	C·H <sub>2</sub> OCH <sub>3</sub> [26]	0±1
H· [22]	52.10±0.001	OH· [22]	8.89±0.09
CH <sub>3</sub> SCH <sub>2</sub> O· [31]	7.4	HOO· [27]	3.50±0.5
C·H <sub>2</sub> OH [28]	-4.08±0.8	CH <sub>3</sub> OCH <sub>3</sub> [29]	-43.99±0.12

Total energies, ZPVE and Thermal Corrections for the standard species used in the working reactions are listed in Table A.1.

**Table 1.3** Total Energies <sup>a</sup> at 298K

Species	B3LYP/ 6-311g(d,p)	ZPVE <sup>b</sup>	Therm. Corr. <sup>c</sup>	CBS-QB3	ZPVE <sup>d</sup>	Therm. Corr. <sup>c</sup>
CH <sub>3</sub> SC·H <sub>2</sub>	-477.3375846	37.77	3.78	-476.7228244	38.11	3.77
CH <sub>3</sub> SCH <sub>2</sub> OOH	-628.3609772	51.71	4.97	-627.5642507	52.19	4.96
CH <sub>3</sub> SCH <sub>2</sub> OO·	-627.7321772	44.43	4.66	-626.9281892	44.83	4.22
C·H <sub>2</sub> SCH <sub>2</sub> OOH	-627.7118901	42.87	5.11	-626.9152611	43.20	5.15
TS1	-627.7018735	41.36	3.87	-626.9009996	41.76	3.86
TS2	-627.7412102	40.62	4.64	-626.8679646	40.97	4.65
TS3	-627.7442828	42.61	4.57	-626.875727	43.06	4.53
TS4	-627.6857737	41.16	5.01	-626.8768683	41.51	5.02
TS5	-627.670856	42.29	4.65	-626.8662235	42.67	4.64

<sup>a</sup> Total energy calculation based on the geometries optimized at B3LYP/6-311g(d,p) level of theory and ZPVE's and thermal corrections to 298k are included. Units in hartree.

<sup>b</sup> ZPVE: scaled zero-point energies in kcal/mol. ZPVE is scaled by 0.9806

<sup>c</sup> Therm.corr.: thermal corrections in kcal/mol

<sup>d</sup> ZPVE: scaled zero-point energies in kcal/mol. ZPVE is scaled by 0.99



**Table 1.4** Reaction Enthalpies at 298K and Calculated Enthalpies of Formation

Isodesmic Reactions	CBS-QB3		B3LYP/6-311g(d,p)	
	$\Delta H_{\text{rxn}}^{\circ}$	$\Delta H_{\text{f}298}^{\circ}$	$\Delta H_{\text{rxn}}^{\circ}$	$\Delta H_{\text{f}298}^{\circ}$
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CH}_3\text{SCH}_3$	2.49	32.65	-0.12	35.27
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{C}\cdot\text{H}_2 + \text{CH}_3\text{SCH}_3$	7.33	30.29	6.01	31.72
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{OC}\cdot\text{H}_2 + \text{CH}_3\text{SCH}_3$	-0.12	35.05	0.42	34.51
$\text{CH}_3\text{SCH}_2\text{OOH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3\text{SCH}_3$	6.42	-29.29	5.76	-28.63
$\text{CH}_3\text{SCH}_2\text{OOH} + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3\text{SCH}_2\text{CH}_3$	3.19	-29.17	3.83	-30.01
$\text{CH}_3\text{SCH}_2\text{OOH} + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{OOH} + \text{CH}_3\text{SCH}_3$	0.57	-28.99	0.65	-29.27
$\text{CH}_3\text{SCH}_2\text{OOH} + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{OOH} + \text{CH}_3\text{SCH}_2\text{CH}_3$	0.017	-29.12	0.36	-29.48
$\text{CH}_3\text{SCH}_2\text{OO}\cdot + \text{CH}_4 \rightarrow \text{CH}_3\text{OO}\cdot + \text{CH}_3\text{SCH}_3$	5.66	5.42	4.57	6.51
$\text{CH}_3\text{SCH}_2\text{OO}\cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{OO}\cdot + \text{CH}_3\text{SCH}_2\text{CH}_3$	2.43	5.54	2.64	5.13
$\text{CH}_3\text{SCH}_2\text{OO}\cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{OO}\cdot + \text{CH}_3\text{SCH}_3$	-0.456	4.94	-0.84	5.13
$\text{CH}_3\text{SCH}_2\text{OO}\cdot + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{OO}\cdot + \text{CH}_3\text{SCH}_2\text{CH}_3$	-1.003	4.80	-1.12	4.92
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} + \text{CH}_4 \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_3 + \text{CH}_3\text{OOH}$	5.68	12.51	5.34	12.85
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} + \text{CH}_3\text{CH}_3 \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_3 + \text{CH}_3\text{CH}_2\text{OOH}$	-0.17	10.46	0.23	10.06

The  $\Delta H_f^\circ_{298}$  for four species show good consistency at the CBS-QB3 level over the several isodesmic reactions used, with the standard deviation for data on  $\text{CH}_3\text{SCH}_2\text{OOH}$  of 0.12kcal/mol. Standard deviations in  $\Delta H_f^\circ_{298}$  values are 0.36 kcal/mol, 1.44kcal/mol for  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  radicals, respectively, where the standard deviation for  $\text{CH}_3\text{SCH}_2\text{OOH}$  molecule is 0.12kcal/mol. And 0.36 kcal/mol, 1.44kcal/mol for  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  radical. The recommended  $\Delta H_f^\circ_{298}$  for the target species are an average of the isodesmic reactions at the CBS-QB3 calculation level. The  $\Delta H_f^\circ_{298}$  are  $-29.14\pm 0.12$ kcal/mol,  $5.17\pm 0.36$ kcal/mol and  $11.48\pm 1.44$ kcal/mol for  $\text{CH}_3\text{SCH}_2\text{OOH}$ ,  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$ , respectively.

Stella et al [30] has estimated the  $\Delta H_f^\circ_{298}$  for  $\text{CH}_3\text{SCH}_2\text{OOH}$  molecule and  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  radical by heats of atomization using UMP2/6-31G(d) level of calculations with value of  $-28.4$ kcal/mol and  $6.51$ kcal/mol, respectively. The  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  radical was calculated relative to the reaction:  $\text{C}\cdot\text{H}_2\text{SCH}_3$  radical plus  $\text{O}_2$ . McKee [31] has calculated the  $\Delta H_f^\circ_{298}$  for  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  at the QCISD(T)/6-31+G(2df,p)//MP2/6-31G(d) level of calculation, giving the value of  $5.9$ kcal/mol, in good agreement with the value of  $5.2$  kcal/mol.  $\Delta H_f^\circ_{298}$  for  $\text{CH}_3\text{SC}\cdot\text{H}_2$  obtained from this work,  $32.66\pm 0.50$  kcal/mol, is  $0.5$ kcal/mol higher than the result of Jefferson's,  $32.1\pm 0.7$ kcal/mol [32].

The accuracy of the enthalpies of formation is controlled by several factors, such as the method and the basis set of the Gaussian analysis; the reliability of the enthalpies of formation of the reference compounds; the uncertainty in the thermal correction; and the choice of the working chemical reactions used in the cancellation of calculation errors.

### 1.3.4 Bond Energies

CH<sub>3</sub>SCH<sub>2</sub>—OOH, CH<sub>3</sub>SCH<sub>2</sub>OO—H, CH<sub>3</sub>SCH<sub>2</sub>O—OH and H—CH<sub>2</sub>SCH<sub>2</sub>OOH bond dissociation energies are presented in Table 1.5. They are estimated using  $\Delta H_f^\circ$  from CBS-QB3 calculation level for CH<sub>3</sub>SCH<sub>2</sub>OOH molecule and its radicals from this work: plus reference radicals.

**Table 1.5** Bond Energies

Reaction series	Bond energy (kcal/mol)
CH <sub>3</sub> SCH <sub>2</sub> —OOH → CH <sub>3</sub> SCH <sub>2</sub> + OOH	65.30
CH <sub>3</sub> SCH <sub>2</sub> O—OH → CH <sub>3</sub> SCH <sub>2</sub> O + OH	45.43
CH <sub>3</sub> SCH <sub>2</sub> OO—H → CH <sub>3</sub> SCH <sub>2</sub> OO + H	86.41
H—CH <sub>2</sub> SCH <sub>2</sub> OOH → CH <sub>2</sub> SCH <sub>2</sub> OOH + H	92.72

### 1.3.5 Entropy and Heat Capacity

Standard entropy ( $S^\circ_{298}$ ) and heat capacities ( $C_p(T)$  ,  $300 \leq T/K \leq 1500$ ) are determined using B3LYP/6-311G(d,p), geometries and harmonic frequencies. The results are summarized in Table 1.6. There are no reported entropy and heat capacity values that we are aware of.

The torsion frequencies are subtracted in the calculation of  $S^\circ_{298}$  and  $C_p(T)$ , but we replace their contributions with values from analysis of the internal rotations. TVR represents the sum of the contributions from translations, external rotations and vibrations for  $S^\circ_{298}$  and  $C_p(T)$  by statistical mechanics. The torsion frequency corresponding to the internal rotor is not included in TVR. Instead, I.R. represent the contribution from hindered internal rotations to  $S^\circ_{298}$  and  $C_p(T)$ . The calculations are based on optimized geometries and rotational potential curves from B3LYP/6-311G(d,p) data. Symmetry and number of optical isomers are incorporated in estimation of  $S^\circ_{298}$  as described in Table 1.6.

**Table 1.6** Ideal Gas- Phase Thermodynamic Properties<sup>a</sup>

Species and( symmetry #)		$\Delta H_f^\circ$ <sup>b</sup>	$S^\circ$ <sup>298</sup> <sup>c</sup>	$C_{p(300)}$ <sup>c</sup>	$C_{p(400)}$ <sup>c</sup>	$C_{p(500)}$ <sup>c</sup>	$C_{p(600)}$ <sup>c</sup>	$C_{p(800)}$ <sup>c</sup>	$C_{p(1000)}$ <sup>c</sup>	$C_{p(1500)}$ <sup>c</sup>
CH <sub>3</sub> SC-H <sub>2</sub> (3) rotors # = 2	TVR <sup>d,i</sup>		64.06	14.27	17.30	19.94	22.16	25.70	28.44	32.95
	I.R.		8.00	3.75	3.71	3.68	3.63	3.46	3.26	2.8
	total	32.66±0.50	72.06	18.02	21.01	23.62	25.79	29.16	31.70	35.75
CH <sub>3</sub> SCH <sub>2</sub> OOH (3) rotors # = 4	TVR <sup>d,i</sup>		69.93	17.21	21.92	26.05	29.48	34.74	38.61	44.70
	I.R. <sup>e</sup>		18.64	7.63	7.82	7.95	8.00	7.80	7.39	6.33
	total	-29.14±0.12	88.57	24.84	29.74	34.00	37.48	42.54	46.00	51.03
CH <sub>3</sub> SCH <sub>2</sub> OO· (3) rotors # = 3	TVR <sup>d,i</sup>		69.88	16.97	21.41	25.27	28.46	33.30	36.79	42.17
	I.R. <sup>e</sup>		17.42	6.22	5.94	5.64	5.35	4.81	4.39	3.76
	total	5.17±0.36	88.68	23.19	27.35	30.91	33.81	38.11	41.18	45.93
C-H <sub>2</sub> SCH <sub>2</sub> OOH (2) rotors # = 4	TVR <sup>d,i,k</sup>		72.96	18.08	22.20	25.62	28.36	32.48	35.49	40.33
	I.R. <sup>e</sup>		16.13	8.10	8.63	8.94	9.04	8.80	8.28	6.94
	total	11.48±1.44	90.47	26.18	30.83	34.56	37.40	41.28	43.77	47.27
TS1 (2) rotors # = 0	TVR <sup>d,k</sup>		75.94	20.99	26.22	30.50	33.89	38.78	42.14	47.07
	I.R.		0	0	0	0	0	0	0	0
	total	22.23	77.33	20.99	26.22	30.50	33.89	38.78	42.14	47.07
TS2 (3) rotors # = 2	TVR <sup>d,k</sup>		73.49	18.64	23.18	27.01	30.12	34.78	38.07	43.00
	I.R.		11.03	3.91	3.79	3.70	3.59	3.31	3.04	2.59
	total	42.96	85.91	22.55	26.97	30.71	33.71	38.09	41.11	45.59
TS3 (3) rotors # = 1	TVR <sup>d,k</sup>		75.51	20.67	24.86	28.45	31.41	35.95	39.26	44.42
	I.R.		5.25	1.73	1.51	1.36	1.27	1.16	1.10	1.04
	total	38.09	82.14	22.40	26.37	29.81	32.68	37.11	40.36	45.46
TS4 (2) rotors # = 3	TVR <sup>d,k</sup>		76.89	20.96	25.06	28.39	31.05	35.01	37.91	42.58
	I.R.		8.74	3.60	3.54	3.42	3.27	2.98	2.73	2.39
	total	35.57	87.01	24.56	28.60	31.81	34.32	37.99	40.64	44.97
TS5 (1) rotors # = 1	TVR <sup>d</sup>		77.09	21.73	26.21	29.77	32.56	36.66	39.64	44.40
	I.R.		4.40	1.15	1.09	1.06	1.04	1.02	1.01	1.00
	total	42.25	82.91	22.88	27.30	30.83	33.60	37.68	40.65	45.40

<sup>a</sup> Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1 atm.<sup>b</sup> Units in kcal/mol. <sup>c</sup> Units in cal/(mol K).<sup>d</sup> The sum of contributions from translations, external rotations, and vibrations. <sup>e</sup> Contribution from internal rotation <sup>f</sup> Contribution from internal rotation about the S—C2 bond. <sup>g</sup> Contribution from internal rotation about the C—O bond. <sup>h</sup> Contribution from internal rotation about the O—O bond. <sup>i</sup> Symmetry number is taken into account(-1.987ln(symmetry number)).<sup>j</sup> Spin degeneracy contribution for entropy=1.987ln(2) is taken into account. <sup>k</sup> optical isomer number is taken into account 1.987ln(2)

### 1.3.6 Group Values and Group Estimation

The C/H2/O/S group is derived from the thermodynamic property data of the target molecule CH<sub>3</sub>SCH<sub>2</sub>OOH. The group value for  $\Delta H_f^{\circ}_{298}$  and  $C_p$  of C/H2/O/S are calculated on the basis of

$$(\text{CH}_3\text{SCH}_2\text{OOH}) = (\text{C/H2/O/S}) + (\text{C/H3/S}) + (\text{S/C/C}) + (\text{O/C/O}) + (\text{O/H/O})$$

and  $S^{\circ}_{298}$  of C/H2/O/S is calculated on the basis of

$$(\text{CH}_3\text{SCH}_2\text{OOH}) = (\text{C/H2/O/S}) + (\text{C/H3/S}) + (\text{S/C/C}) + (\text{O/C/O}) + (\text{O/H/O}) - R \ln(\sigma) + R \ln(\text{OI})$$

where  $R=1.987\text{cal/mol K}$ ,  $\sigma$  is symmetry number and OI stands for the optical isomer number. Selection of the initial group values is critical to development of group additivity for accurate property estimation. The C/H2/O/S group value derived in this work are listed in Table 1.7

### 1.3.7 Hydrogen Bond Increment Group Value for Radicals

This method utilizes the thermodynamic properties of the parent molecules incorporated with a H atom bond increment (HBI) to estimate thermochemical properties of radicals where a H atom is removed.

HBI group values for CH<sub>3</sub>SCH<sub>2</sub>OO· and C·H<sub>2</sub>SCH<sub>2</sub>OOH are derived from thermodynamic property data of CH<sub>3</sub>SCH<sub>2</sub>OOH molecule and its two radicals. The HBI group for  $\Delta H_f^{\circ}_{298}$  component reflects the enthalpy change due to loss of a H atom [34] from a stable parent molecule in the form of the R-H bond energy. For example, the bond energy of CH<sub>3</sub>SCH<sub>2</sub>OO-H is based on the heat of reaction of the following reaction:

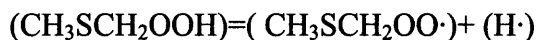
**Table 1.7** Group Value

Groups	$\Delta H_f^\circ_{298}$ <sup>a</sup>	$S^\circ_{298}$ <sup>b</sup>	$C_p(300)$ <sup>b</sup>	$C_p(400)$ <sup>b</sup>	$C_p(500)$ <sup>b</sup>	$C_p(600)$ <sup>b</sup>	$C_p(800)$ <sup>b</sup>	$C_p(1000)$ <sup>b</sup>	$C_p(1500)$ <sup>b</sup>
CH <sub>3</sub> SCH <sub>2</sub> OOH	-29.14	88.57	24.84	29.74	34.00	37.48	42.54	46.00	51.03
C/H3/S	-10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
S/C/C	11.51	13.15	4.99	4.96	5.02	5.07	5.41	5.73	5.70
O/C/O	-5.5	8.54	3.90	4.31	4.60	4.84	5.32	5.80	6.01
O/H/O	-16.30	27.83	5.21	5.72	6.17	6.66	7.15	7.61	8.43
C/H2/O/S	-8.77	9.39	4.55	6.91	8.81	10.12	11.64	12.09	13.31

<sup>a</sup>Units in kcal/mol. <sup>b</sup> Units in cal/(mol K)<sup>c</sup> reference [33]**Table 1.8** HBI Group Values for CH<sub>3</sub>SCH<sub>2</sub>OO· and C·H<sub>2</sub>SCH<sub>2</sub>OOH Radicals

	Bond Energy <sup>a</sup>	$S^\circ_{298}$ <sup>b</sup>	$C_p(300)$ <sup>b</sup>	$C_p(400)$ <sup>b</sup>	$C_p(500)$ <sup>b</sup>	$C_p(600)$ <sup>b</sup>	$C_p(800)$ <sup>b</sup>	$C_p(1000)$ <sup>b</sup>	$C_p(1500)$ <sup>b</sup>
CH <sub>3</sub> SCH <sub>2</sub> OO·	86.4	0.11	-0.65	-2.39	-3.09	-3.67	-4.43	-4.82	-5.10
C·H <sub>2</sub> SCH <sub>2</sub> OOH	92.7	1.15	0.59	1.09	0.56	-0.08	-1.26	-2.23	-3.76

<sup>a</sup>Units in kcal/mol. <sup>b</sup> Units in cal/(mol K)



$\Delta H^\circ_{\text{rxn}} = D(\text{CH}_3\text{SCH}_2\text{OO-H})$  The bond energy of  $\text{CH}_3\text{SCH}_2\text{OO-H}$  can be described as

$$D(\text{CH}_3\text{SCH}_2\text{OO-H}) = (\text{CH}_3\text{SCH}_2\text{OO}\cdot) + 52.1 - (\text{CH}_3\text{SCH}_2\text{OOH})$$

HBI group for heat capacity is more simply described as

$$\text{HBI } C_p(\text{T}) \text{CH}_3\text{SCH}_2\text{OO}\cdot = C_p(\text{T}) \text{CH}_3\text{SCH}_2\text{OO}\cdot - C_p(\text{T}) \text{CH}_3\text{SCH}_2\text{OOH}$$

The effects for changes in symmetry between the radical and parent are not included in the HBI group but are included in evaluation of the entropy of each species separately. The HBI group value of  $S^\circ_{298}$  is therefore termed intrinsic (Benson) and can be written as

$$\begin{aligned} \text{HBI}(S^\circ_{298})\text{CH}_3\text{SCH}_2\text{OO}\cdot &= S^\circ_{298}\text{CH}_3\text{SCH}_2\text{OO}\cdot + R \ln \sigma(\text{CH}_3\text{SCH}_2\text{OO}\cdot) - \\ &S^\circ_{298}\text{CH}_3\text{SCH}_2\text{OOH} - R \ln(\sigma) (\text{CH}_3\text{SCH}_2\text{OOH}) \end{aligned}$$

### 1.3.8 Thermochemical Kinetic Analysis of the Reaction

**1.3.8.1  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow (\text{CH}_3\text{SCH}_2\text{OO}\cdot)^* \rightarrow \text{Products}$ .** A potential energy diagram for the methylthiomethyl radical with  $\text{O}_2$  is illustrated in Figure 1.6; energies are calculated at the CBS-QB3 level. Addition of oxygen to the  $\text{CH}_3\text{SC}\cdot\text{H}_2$  radical forms an energized adduct which can react to new products.



Possible reactions for this activated adduct are described as follows:



Rxn3: Hydrogen atom shift from the methyl group to form an energized hydroperoxide methyl radical:



Rxn4: Hydrogen atom transfer from peroxy carbon (TS2)



The  $\text{CH}_3\text{SC}\cdot\text{HOOH}$  is unstable and immediately dissociates to  $\text{CH}_3\text{SC}(=\text{O})\text{H}$  plus OH radical (TS2)

Rxn5: The oxygen radical on this peroxy radical can also attack the sulfur atom to form a cyclic transition state structure (TS3, a 4-member ring) where the relatively strong S=O bond (near double bond) starts to form; and the weak (SO—OC) peroxide bond in the transition state starts to cleave (ring opening). The initial product from this reaction: a radical intermediate  $\text{CH}_3\text{S}(=\text{O})\text{CH}_2\text{O}\cdot$  will undergo beta scission (carbonyl formation) resulting in  $\text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$

The methylthiomethyl radical ( $\Delta H_f^\circ_{298} = 32.66$  kcal/mol) adds to  $\text{O}_2$  to form  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  peroxy radical ( $\Delta H_f^\circ_{298} = 5.17$  kcal/mol). The transition state for H atom shift from the methyl ( $\text{CH}_3$ ) carbon (6 member ring tst) has a barrier (activation energy) of 17.06 kcal/mol, thus TS1 is below the entrance channel of the reactants.  $\Delta H_f^\circ_{298}$  for the  $\text{CH}_3\text{SC}\cdot\text{HOOH}$  radical in Reaction 4 is estimated on the base of the result of  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  and their difference of total energy calculated under MP2/6-31G(d,p) level. The activated  $\text{CH}_3\text{SCH}_2\text{OO}\cdot^*$  adduct crossed TS2, which then undergoes OH elimination to form  $\text{CH}_3\text{SC}(=\text{O})\text{H}$ , with the barrier 37.79 kcal/mol. Reaction 5 has a barrier of 32.92 kcal/mol.



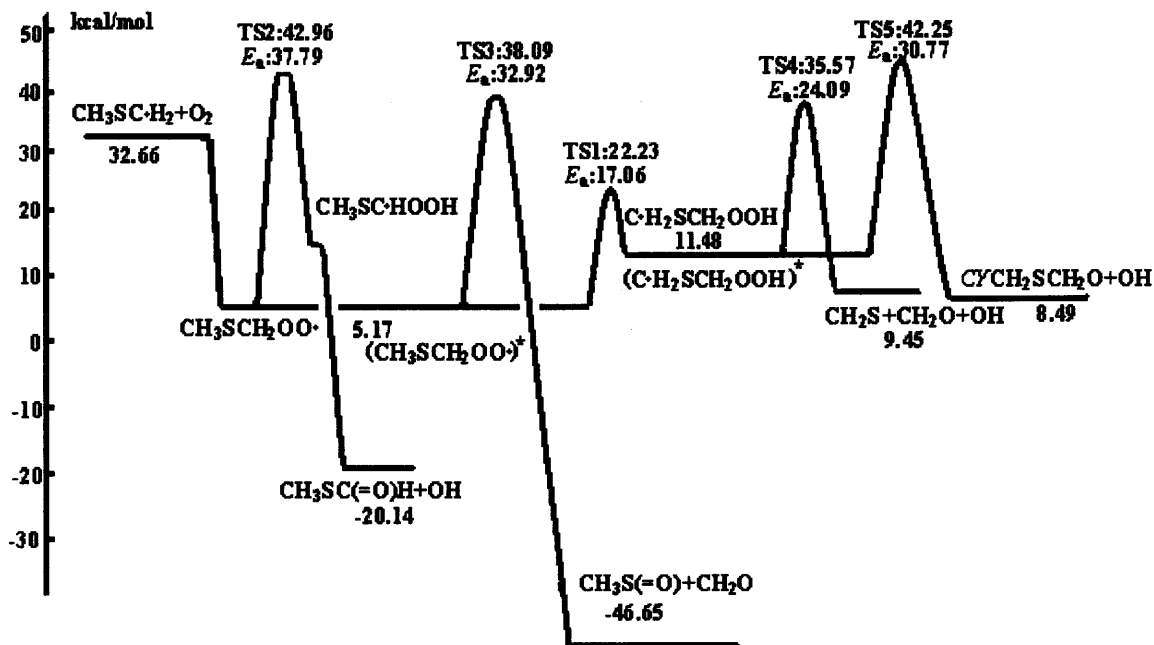


Figure 1.6 Potential energy diagram  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$ .

1.3.8.2  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}^* \rightarrow \text{Products}$ . The energized  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  can undergo four different reactions:

Rxn1: Reverse reaction-back to  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  radical.

Rxn2: Stabilization.

Rxn3: Beta scission reaction to  $\text{CH}_2=\text{S} + \text{C}\cdot\text{H}_2\text{OOH}$  radical. The  $\text{C}\cdot\text{H}_2\text{OOH}$  radical has little or no barrier to dissociation cleaving a weak  $\text{CO}-\text{OH}$  bond (ca 45 kcal-mol<sup>-1</sup>) and forming a strong carbonyl bond (~80 kcal-mol<sup>-1</sup>) + OH radical. The activation energy of TS4 is 24.1 kcal/mol.

Rxn4: Cyclization forming through TS5 where the  $\text{sp}^3$  carbon based radical attaches the C-O peroxide oxygen through a four-member ring transition state (TS5) to form 1,3-Oxathietane + OH. The activation energy of TS5 is 30.8 kcal/mol, based on the CBS-QB3 level of theory.

**Table 1. 9** High-Pressure Limit Rate Constants as Input Parameters for QRRK-Master Equation Calculations

	Reaction	$A(\text{s}^{-1})$	$n$	$E_a$ (kcal/mol)
$k_1$	$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{OO}\cdot$	5.82E+12	0.00	0.00
$k_{-1}$	$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$	4.28E+14	0.00	26.90
$k_2$	$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$	1.22E+07	1.20	17.06
$k_{-2}$	$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CH}_3\text{SCH}_2\text{OO}\cdot$	7.55E+10	-0.26	10.75
$k_3$	$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$	8.31E+09	0.92	37.79
$k_4$	$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$	1.70E+10	0.53	32.92
$k_5$	$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$	6.45E+13	-0.47	24.09
$k_6$	$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CYCH}_2\text{SCH}_2\text{O} + \text{OH}$	3.72E+13	-0.70	30.77

Results are calculated using Thermkin Program.

Lennard-Jones parameters:  $\sigma = 5.54 \text{ \AA}$ ,  $\epsilon/k = 460$  Geometric mean frequency

(from CPFIT, :  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  ( $904.0 \text{ cm}^{-1} \times 22.5$ ),  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  ( $736.9 \text{ cm}^{-1} \times 23.0$ ))

$k_{-1}$ ,  $k_{-2}$ : microscopic reversibility MR

$k_2$ ,  $k_3$ ,  $k_4$ ,  $k_5$ ,  $k_6$  fitting with three-parameter modified Arrhenius equation over the temperature range from 200 to 2000 K using THERMKIN (a canonical transition calculation for the rate constant from the thermochemical data on the reactants and corresponding transition state.)

**Table 1.10** Resulting Rate Constants in QRRK Calculations  
 Calculated Reaction Parameters at P=1 atm,  $k = A(T)^n \exp(-E_a/RT)$  (T=200-2000k)

Reaction	$A(\text{s}^{-1})$	$n$	$E_a$ (kcal/mol)	$k_{298}$ ( $\text{s}^{-1}$ )
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{OO}\cdot$	3.697E+64	-17.25	11.64	5.738E+12
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$	8.734E+67	-18.52	15.54	7.872E+09
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$	9.563E+09	0.35	11.82	1.582E+02
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$	3.546E+11	-0.37	8.13	4.435E+04
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$	9.149E+17	-1.97	10.75	7.453E+04
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CYCH}_2\text{SCH}_2\text{O} + \text{OH}$	2.227E+15	-1.65	14.80	1.639E+00
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$	8.265E+40	-8.98	32.14	8.269E-06
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$	3.267E+46	-12.39	43.46	8.275E-17
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$	1.169E+43	-10.99	38.74	2.069E-13
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$	1.550E+31	-6.39	27.65	9.274E-06
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CYCH}_2\text{SCH}_2\text{O} + \text{OH}$	3.065E+36	-8.60	35.28	1.541E-11

### 1.3.9 QRRK Calculation Results

$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{Products}$ : QRRK calculations for  $k(E)$  and master equation analysis for fall-off are performed on  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$  reaction system and results are list in Table 1.9 and Table 1.10.

In all calculations  $\Delta E_{\text{down}}$  of 830 cal/mol is used. Rate constant at 298K and 1000K versus Pressure are illustrated in Figure 1.7 and Figure 1.8.

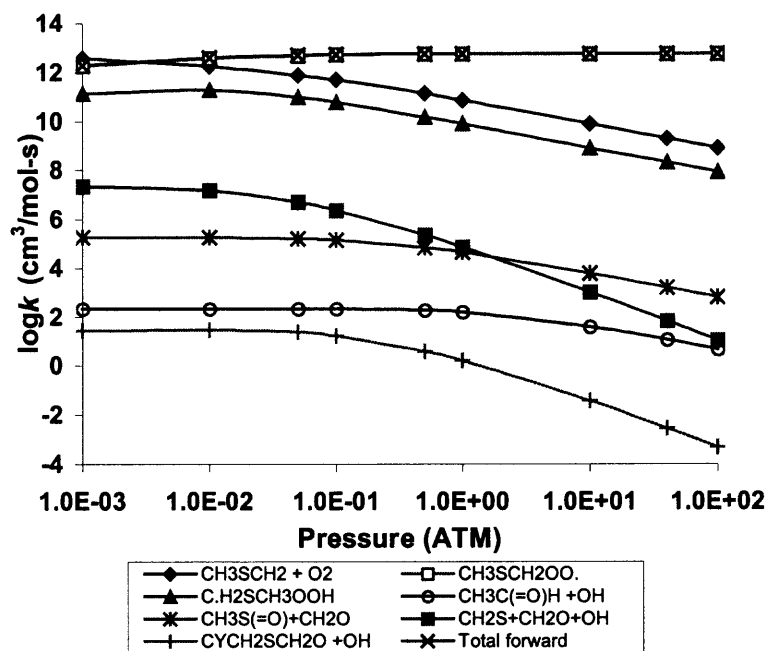


Figure 1.7  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{Products}$   $\log k$  vs. pressure at 298K.

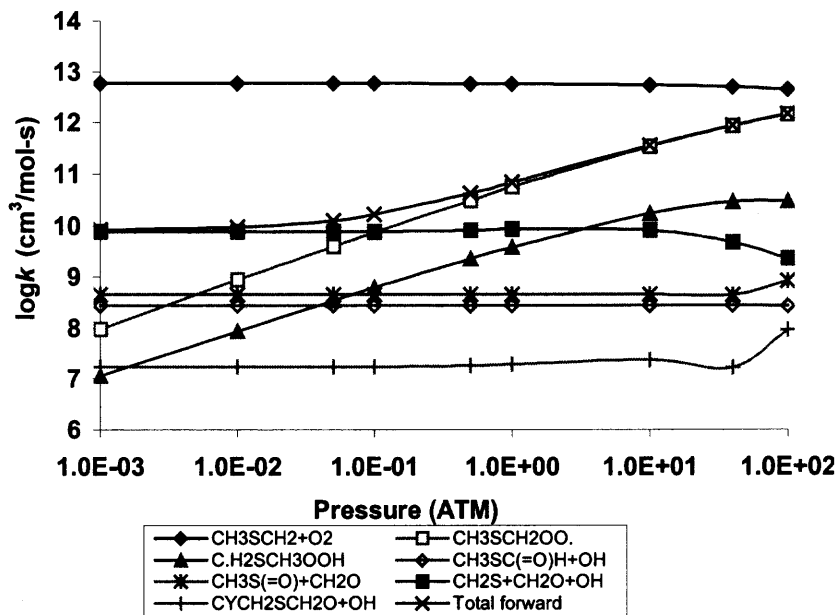


Figure 1.8  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{Products}$   $\log k$  vs. pressure at 1000K.

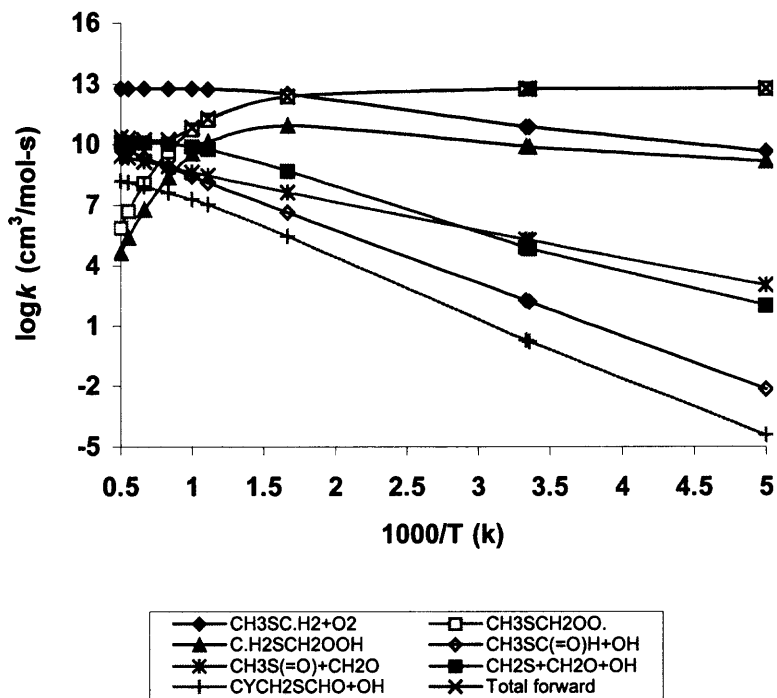


Figure 1.9  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{Products}$   $\log k$  vs. temperature at 1 atm.

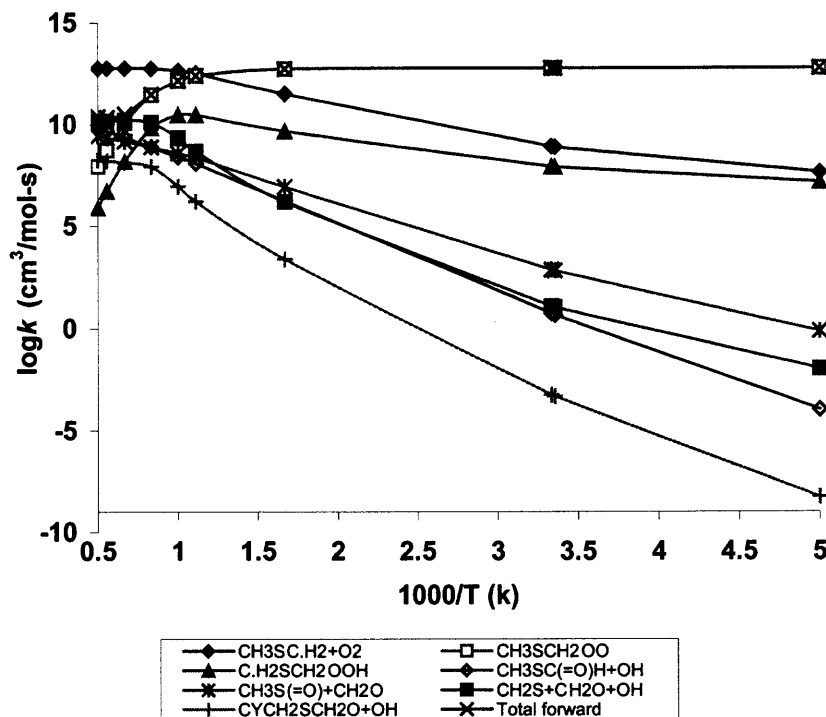


Figure 1.10  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{Products}$   $\log k$  vs. temperature at 100 atm.

At 298 K, stabilization  $[\text{CH}_3\text{SCH}_2\text{OO}\cdot]$  is the dominant reaction over 0.01atm, and the rate constants for  $\text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$  and  $\text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$  products are similar over the entire pressure range at 298K. Dissociation to  $\text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$  is the major reaction below 0.1atm at 1000K. Plots of calculated rate constants for  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$  at 1atm and 100 atm  $\log k$  versus  $1000/T$  are illustrated in Figure 1.9 and Figure 1.10. Stabilization to  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  is the dominant reaction below 1100K and this crossover temperature is shifted to 1500K at 100 atm.

Unimolecular Dissociation Reactions of the Stabilized Adducts:

1.  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  Dissociation: Plots of rate constants for  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  dissociation at 1 atm pressure  $1000/T$  and of rate constants at 1000K versus pressure are illustrated in Figure 1.11 and Figure 1.12.  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  stabilization are

important at the entire temperature range. At 1000K,  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$  and  $\text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$  products increase as pressure is increased.

2.  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  Dissociation: Rate constants for  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  dissociation at 1 atm pressure versus  $1000/T$  and rate constants at 1000K versus pressure are illustrated in Figure 1.13 and Figure 1.14. Isomerization to  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  is the dominant reaction path at low pressure. The  $\text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$  products are important at high pressure.

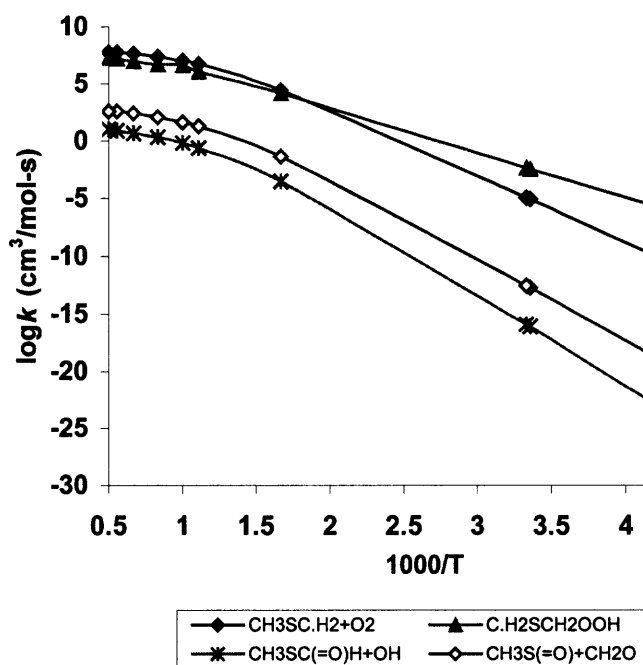


Figure 1.11  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  Dissociation  $\log k$  vs. temperature at 1 atm.

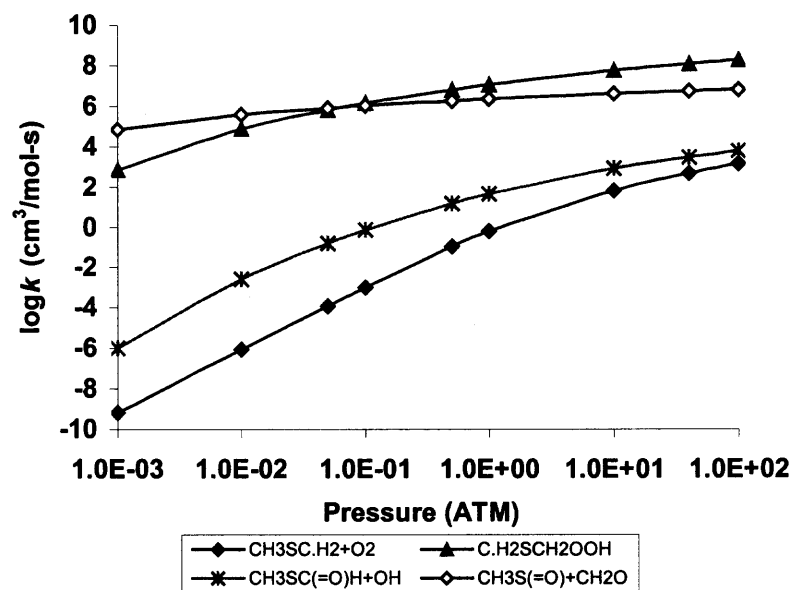


Figure 1.12  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  Dissociation  $\log k$  vs. pressure at 1000K.

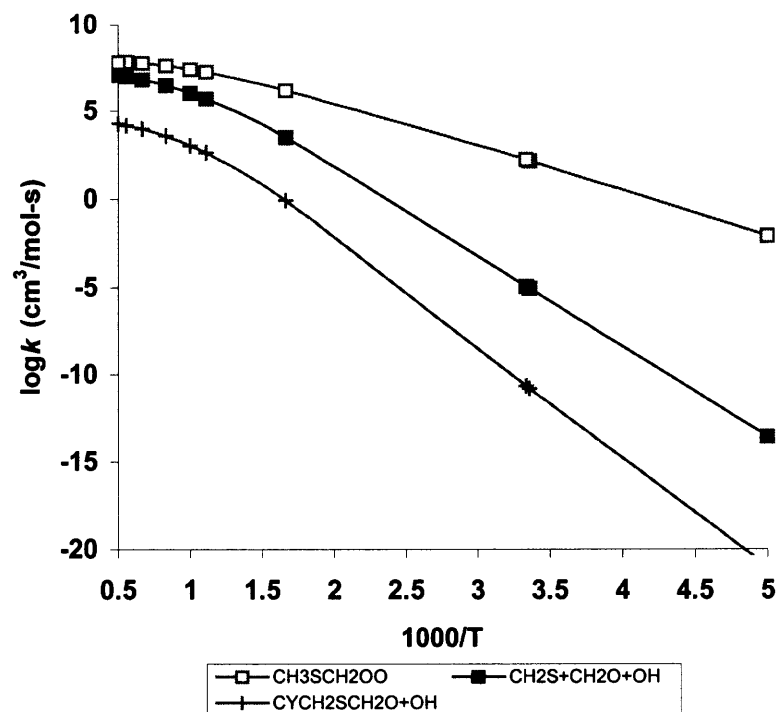


Figure 1.13  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  Dissociation  $\log k$  vs. temperature at 1 atm.



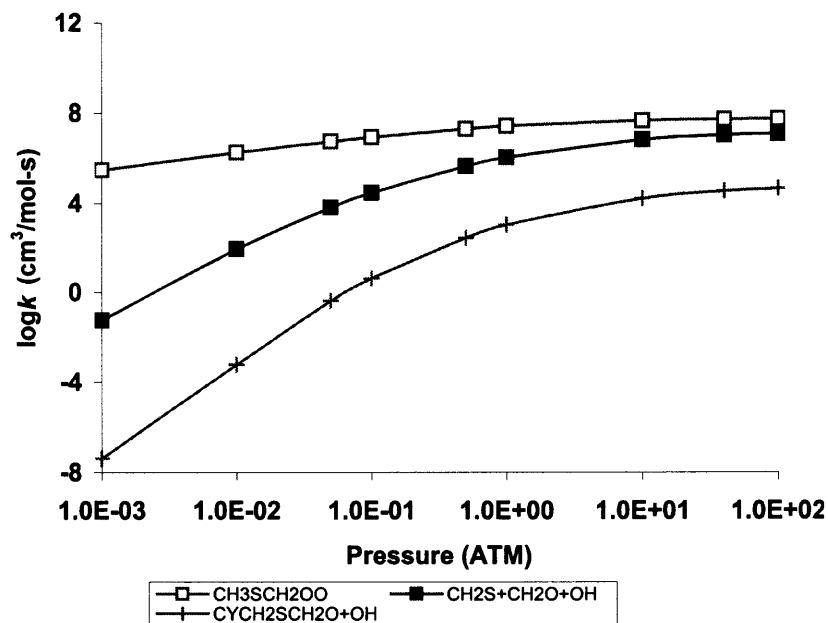


Figure 1.14 C·H<sub>2</sub>SCH<sub>2</sub>OOH Dissociation log *k* vs. pressure at 1000K.

#### 1.4 Summary

Thermodynamic Properties of stable radicals and transition states are calculated on the CH<sub>3</sub>SC·H<sub>2</sub> + O<sub>2</sub> association reaction system using density functional method and CBS-QB3 method.  $\Delta H_f^{\circ}_{298}$  for stable radicals CH<sub>3</sub>SC·H<sub>2</sub>, CH<sub>3</sub>SCH<sub>2</sub>OO· and C·H<sub>2</sub>SCH<sub>2</sub>OOH are estimated using total energies and isodesmic reaction with ZPVE's and thermal correction. The  $\Delta H_f^{\circ}_{298}$  of transition states are estimated by evaluation of  $\Delta H_f^{\circ}_{298}$  of the stable radical adducts plus the difference of the total energies with ZPVE's and thermal correction between these radical species and the transition state's

Entropies ( $S^{\circ}_{298}$ ) and heat capacities ( $C_p(T)$ ,  $300 \leq T/K \leq 1500$ ) are determined with BLYP/6-311g(d,p) optimized geometries and frequencies, considering hindered internal rotation contributions to entropy and heat capacity. The thermodynamic

properties of C/H2/S/O group are determined using group additivity analysis. The group increment values for  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$  are also determined.

Reaction pathway and kinetics are analyzed on the  $\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$  reaction system using QRRK for  $k(E)$  and a master equation fall-off. Reaction to products is evaluated versus both pressure and temperature. Stabilization  $\text{CH}_3\text{SCH}_2\text{OO}\cdot$  is the dominant reaction below 1100K at 1 atm.  $\text{CH}_2\text{S}+\text{CH}_2\text{O}+\text{OH}$  is the major reaction above 1500K.

**CHAPTER 2**  
**STRUCTURES, THERMOCHEMICAL PROPERTIES, INTERNAL ROTATION**  
**BARRIERS AND ENERGIES OF SULFENIC ACIDS, ETHENETHIOL AND**  
**SULFENIC ESTER**

**2.1 Introduction**

Sulfenic acids are organosulfur oxyacids of the form RSOH, where R is an organic moiety [35-37]. These species are important reactive intermediates in the biologically important oxidation of thiols [38,39]. Unlike the more highly oxidized sulfinic and sulfonic acids, which are relatively stable, sulfenic acids are generally unstable and highly reactive compounds [40]. In large part this is due to the high nucleophilicity of the sulfur atom. When considered with the electrophilicity of the organic R group, this nucleophilicity accounts for the tendency of sulfenic acids to undergo self-condensation to form the thiosulfinate [41].



The simplest sulfenic acid (CH<sub>3</sub>SOH) presumably plays a role in the photochemical oxidative degradation of methanethiol and dimethyl disulfide [42-45]. CH<sub>3</sub>SOH has been generated in the gas phase by thermolysis of methyl *tert*-butyl sulfoxide and its structure determined from microwave spectra [46,47].

Experimental thermochemical data ( $\Delta H_f^\circ_{298}$ ) of methanesulfenic acid CH<sub>3</sub>SOH and its cation radical are initially reported as -45.45 and 163.87 kcal/mol [48]. Dewar evaluated the reaction enthalpies of decompositions of methanesulfenic acid and its cation radical utilizing collisionally activated dissociation, neutralization reionization, tandem mass spectrometric techniques and MNDO calculations [49]. Turecek et al.

reported the theoretical heat formation of  $\text{CH}_3\text{SOH}$  is  $-42.82\text{kcal/mol}$  under MNDO method. Atomization method was used to estimate the  $\Delta H_f^\circ$  of simple sulfenic acids ( $\text{CH}_3\text{SOH}$ :  $-35.6\text{kcal/mol}$ ) and their radicals ( $\text{CH}_3\text{SO}\cdot$ :  $-17.8\text{kcal/mol}$ ) by Gregory and Jenks [50], and they also concluded that the sulfinyl radical ( $\text{RSO}\cdot$ ) appears to be the best radical stabilizing group of the four radicals ( $\text{RSO}\cdot$ ,  $\text{RSS}\cdot$ ,  $\text{ROO}\cdot$ ,  $\text{ROS}\cdot$ ).

Block [51] studied methanesulfenic acid ( $\text{CH}_3\text{SOH}$ ) and found that it was generated in the gas phase by thermolysis of methyl *tert*-butyl sulfoxide. And its structure determined from microwave spectra.

In this chapter, enthalpy ( $\Delta H_f^\circ$ ) and heat capacities ( $C_p(T)$ ) are determined for the a series of representative sulfenic acids and their radicals using CBS-QB3 method. Enthalpies of formation are evaluated using isodesmic working reactions. Contributions to entropy and heat capacities from internal rotation are estimated, with B3LYP/6-311g(d,p) level calculations for rotation barrier.

## 2.2 Calculation Method

All the calculations were performed using the Gaussian 98 program suit. The structure parameters are fully optimized at the B3LYP/6-311G(d,p) level of theory. The harmonic vibration frequencies and zero-point vibration energies (ZPVE) are computed at the same level. The total energies are corrected by ZPVE's, which are scaled by 0.99.

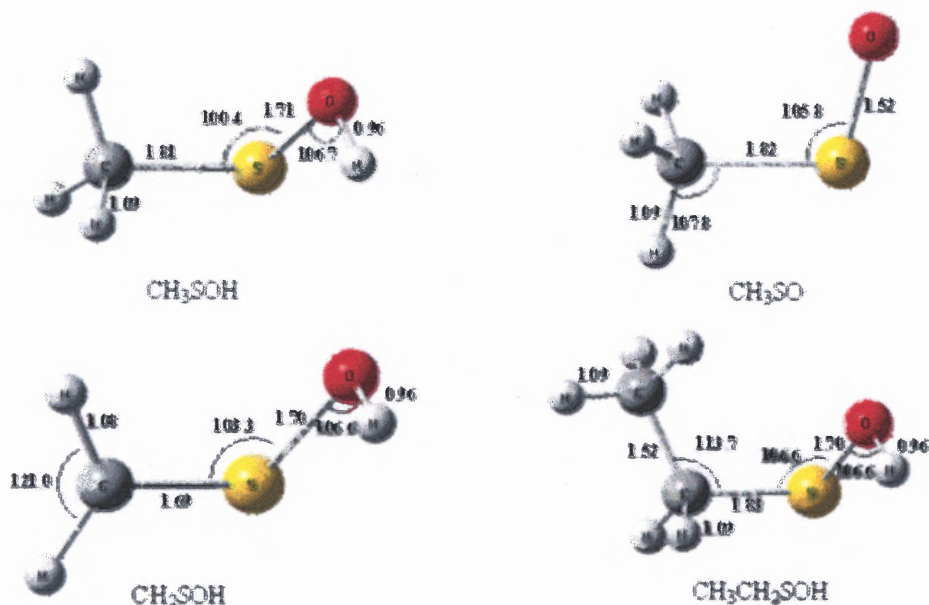
Enthalpies of formation ( $\Delta H_f^\circ$ ) are calculated using total energies and isodesmic reactions. Isodesmic reactions are hypothetical reactions where the number of electron pairs and the bonds of the same type are conserved on both sides of the equation; only the relationship among the bonds is altered.

Entropies and heat capacities at temperature range from 300K to 1500K were calculated using the rigid – rotor- harmonic – oscillator approximation based on scaled vibrational frequencies and moments of inertia of the optimized B3LYP/6-311G(d,p) structures.

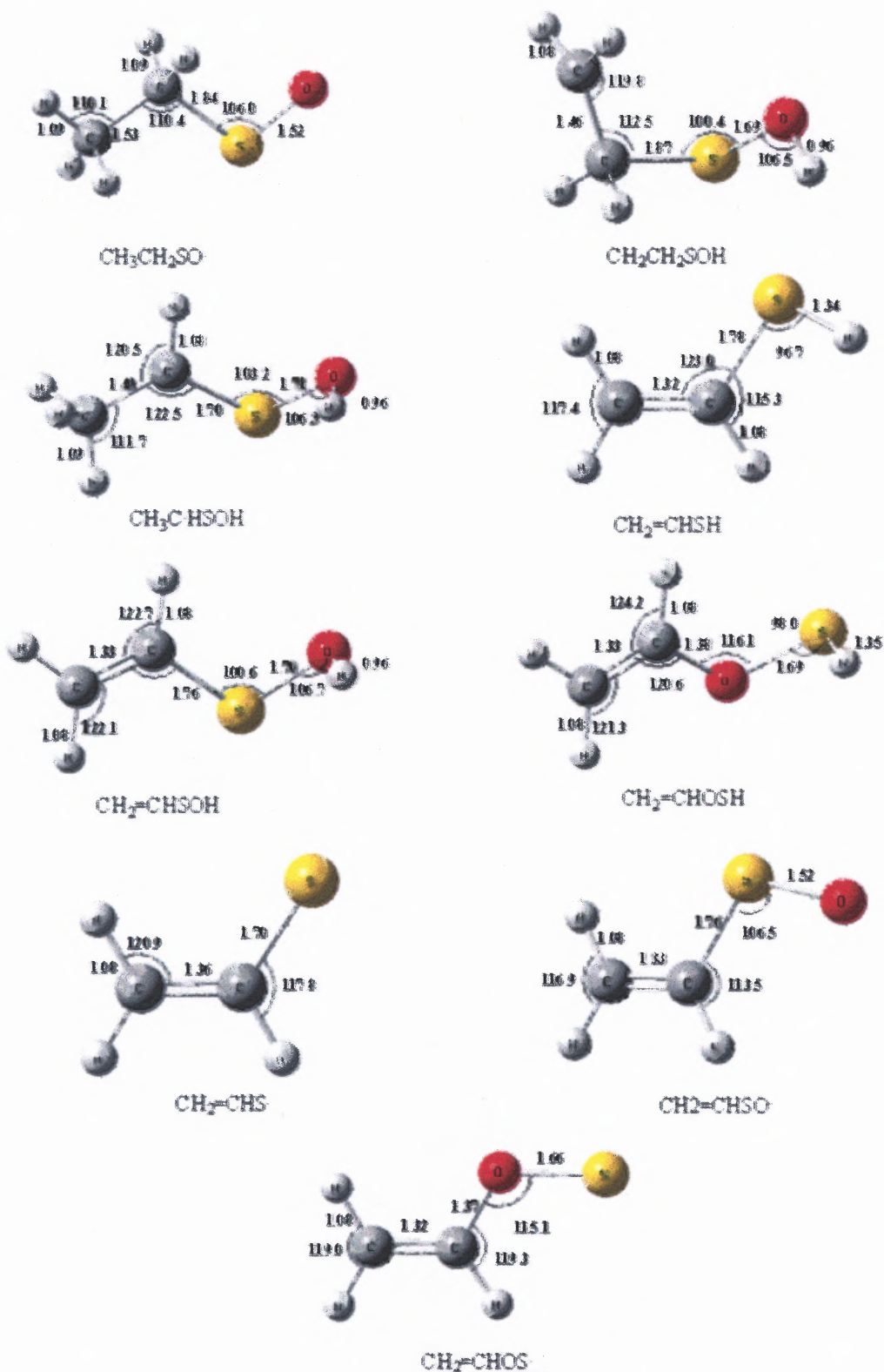
## 2.3 Results and Discussion

### 2.3.1 Geometries and Vibrational Frequencies

The optimized geometries of the target species, obtained at B3LYP/6-311G(d,p) levels of theory, are depicted in Figure.2.1 with geometric parameters. Vibrational frequencies and moments of inertia are list in Table 2.1.



**Figure 2.1** Structures and geometrical parameters for all species studied at B3LYP/6-311G(d,p) Distance is present in Å and angles in degrees.



**Figure 2.1** Structures and geometrical parameters for all species studied at B3LYP/6-311G(d,p) Distance is present in Å and angles in degrees. (Continued)

For the stable molecules:  $\text{CH}_3\text{SOH}$  and  $\text{CH}_3\text{CH}_2\text{SOH}$ , the bond length of S-O is about 1.70 Å, much longer than the result (1.63 Å) calculated by McKee [52] under the MP2/6-31+G(d) level, whereas the S-O bondlength in  $\text{CH}_3\text{SO}\cdot$  radical is 1.52 Å which represents the character of partial double bond.

**Table 2.1** Vibration Frequencies and Moments of Inertia

	Moments of inertia (amu Bohr <sup>2</sup> )	Frequencies (cm <sup>-1</sup> )
$\text{CH}_3\text{SOH}$	88.20335 231.02327 302.03357	187, 287, 408, 686, 728, 975, 980, 1175, 1354, 1449, 1481, 30301, 3112, 3125, 3788
$\text{CH}_3\text{SO}\cdot$	67.91437 218.87298 275.30467	141, 323, 659, 903, 956, 1000, 1335, 1446, 1463, 3037, 3132, 31334
$\text{C}\cdot\text{H}_2\text{SOH}$	74.57081 213.69217 278.66335	289, 315, 391, 534, 672, 831, 918, 11489, 1395, 3133, 3259, 3759
$\text{CH}_3\text{CH}_2\text{SOH}$	177.79481 440.36096 548.99680	118, 201, 278, 371, 429, 638, 719, 778, 974, 1057, 1072, 1169, 1269, 1311, 1412, 1459, 1488, 1506, 3026, 3032, 3068, 3096, 3117, 3789
$\text{CH}_3\text{CH}_2\text{SO}\cdot$	84.09157 546.70323 608.22638	59, 208, 212, 367, 658, 767, 980, 999, 1004, 1064, 1249, 1280, 1418, 1471, 1497, 1502, 3033, 3051, 3089, 3102, 3110
$\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$	171.40402 427.81618 528.99931	110, 174, 264, 344, 420, 538, 652, 721, 768, 1035, 1074, 1173, 1223, 1263, 1448, 1475, 3034, 3089, 3146, 3251, 3786
$\text{CH}_3\text{C}\cdot\text{HSOH}$	97.97550 557.07868 614.13046	75, 135, 238, 318, 384, 583, 643, 732, 992, 1023, 1097, 1143, 1306, 1405, 1469, 1488, 2988, 3024, 3091, 3156, 3760

**Table 2.1** Vibration Frequencies and Moments of Inertia.(Continued.)

	Moments of inertia (amu Bohr <sup>2</sup> )	Frequencies (cm <sup>-1</sup> )
CH <sub>2</sub> =CHSH	36.31178 311.77839 345.55213	157, 365, 596, 696, 916, 929, 987, 1067, 1304, 1419, 1659, 2671, 3139, 3171, 3225
CH <sub>2</sub> =CHSOH	95.20691 505.46448 571.41962	107, 222, 391, 431, 616, 719, 725, 927, 985, 1046, 1175, 1283, 1417, 1642, 3134, 3155, 3221, 3782
CH <sub>2</sub> =CHOSH	48.03702 623.51757 648.40224	68, 283, 292, 449, 704, 724, 873, 944, 982, 993, 1162, 1329, 1414, 1696, 2595, 3151, 3165, 3252
CH <sub>2</sub> =CHS·	31.58568 291.24936 322.83504	401, 465, 765, 933, 966, 1049, 1291, 1359, 1517, 3122, 3134, 3232
CH <sub>2</sub> =CHSO·	65.69148 490.52500 556.21648	105, 237, 423, 540, 678, 923, 984, 1005, 1021, 1261, 1410, 1608, 3134, 3167, 3223
CH <sub>2</sub> =CHOS·	35.07602 609.90150 644.97743	110, 281, 458, 698, 769, 900, 965, 982, 1140, 1318, 1410, 1663, 3160, 3176, 3260

### 2.3.2 Enthalpies of Formation ( $\Delta H_f^\circ_{298}$ )

The enthalpies of formation ( $\Delta H_f^\circ_{298}$ ) of the species concerned in this chapter are estimated using total energies and calculated  $\Delta H_{\text{rxn}298}$  for the listed reactions. The total energies are determined at the CBS-QB3 level; scaled ZPVE's and thermal corrections to 298.15K are listed in Table 2.2.



**Table 2.2** Total Energies <sup>a</sup> at 298K

Species	CBS-QB3	ZPVE <sup>b</sup>	Therm. Corr <sup>c</sup>
CH <sub>3</sub> SOH	-513.2741601	32.16	3.42
CH <sub>3</sub> SO·	-512.6677098	24.75	3.23
C·H <sub>2</sub> SOH	-512.6276196	23.56	3.38
CH <sub>3</sub> CH <sub>2</sub> SOH	-552.5003207	50.00	4.15
CH <sub>3</sub> CH <sub>2</sub> SO·	-551.8924374	42.60	4.04
C·H <sub>2</sub> CH <sub>2</sub> SOH	-551.8406335	40.94	4.32
CH <sub>3</sub> C·HSOH	-551.8548475	41.16	4.37
CH <sub>2</sub> =CHSH	-476.1645732	31.57	3.27
CH <sub>2</sub> =CHSOH	-551.2901117	35.35	3.85
CH <sub>2</sub> =CHOSH	-551.2769922	34.09	3.86
CH <sub>2</sub> =CHS·	-475.5394689	25.80	2.87
CH <sub>2</sub> =CHSO·	-550.6846759	27.93	3.62
CH <sub>2</sub> =CHOS·	-550.6561673	28.70	3.50

<sup>a</sup> Total energy calculation based on the geometries optimized at B3LYP/6-311g(d,p) level of theory and ZPVE's and thermal corrections to 298K are included. Units in hartree.

<sup>b</sup> ZPVE: scaled zero-point energies in kcal/mol. ZPVE is scaled by 0.99

<sup>c</sup> Therm.corr.: thermal corrections in kcal/mol.

The  $\Delta H_f^{\circ}_{298}$  for sulfenic acids molecule (CH<sub>3</sub>SOH, CH<sub>3</sub>CH<sub>2</sub>SOH, CH<sub>2</sub>=CHSOH), ethenethiol (CH<sub>2</sub>=SH), sulfenic ester (CH<sub>2</sub>=CHOSH) and their radicals (CH<sub>3</sub>SO·, C·H<sub>2</sub>SOH, CH<sub>3</sub>CH<sub>2</sub>SO·, C·H<sub>2</sub>CH<sub>2</sub>SOH, CH<sub>3</sub>C·HSOH, CH<sub>2</sub>=CHSO·, CH<sub>2</sub>=CHS·, CH<sub>2</sub>=CHOS·) are determined from total energies and isodesmic reactions. All four compounds in each reaction are estimated using density functional and CBS-QB3 calculations. ZPVE's and thermal correction are taken into account. And the enthalpy of reaction ( $\Delta H^{\circ}_{\text{rxn}}$ ) is obtained. Since  $\Delta H_f^{\circ}_{298}$  of other three compounds have been experimentally determined or theoretically calculated, the unknown enthalpies of the target species are calculated. Enthalpies of formation and their corresponding

uncertainties for standard species used in the isodesmic working reactions are obtained from evaluation of literature data. The values are listed in Appendix Table 1.

### 2.3.2.1 Methanesulfenic Acid (CH<sub>3</sub>SOH) and Its Radicals.

The reaction enthalpies and  $\Delta H_f^\circ_{298}$  for the methanesulfenic acid and its radicals obtained from the reaction schemes are tabulated in Table 2.3. The results for  $\Delta H_f^\circ_{298}$  show very good consistency over working reactions. The  $\Delta H_f^\circ_{298}$  values for target radicals are based on the  $\Delta H_f^\circ_{298}$  values of the parent molecules in this work. The calculated enthalpy for CH<sub>3</sub>SOH is  $-34.70 \pm 0.48$  kcal/mol, which is in agreement with the reference data  $-33.34$  kcal/mol by Wang et al.

Comparing with the reference data, the value for CH<sub>3</sub>SO· ( $\Delta H_f^\circ_{298} = -18.95 \pm 0.59$  kcal/mol) in this work is much larger than the experimental value  $-14.8$  kcal/mol. The  $H_f^\circ_{298}$  for C·H<sub>2</sub>SOH is  $6.44 \pm 0.30$  kcal/mol. There are no reported  $\Delta H_f^\circ_{298}$  values that we are aware of.

The stability of this C·H<sub>2</sub>SOH radical can be evaluated, in part, by its  $\Delta H_{\text{rxn}}$  for the following



### 2.3.2.2 Ethanesulfenic Acid (CH<sub>3</sub>CH<sub>2</sub>SOH) and Its Radicals.

There is a lack of experimental and theoretical data on the enthalpies of formation of CH<sub>3</sub>CH<sub>2</sub>SOH and its radicals. We estimate these data using isodesmic reaction listed in Table 2.4. The  $\Delta H_f^\circ_{298}$  values for ethanesulfenic acid are based on the  $\Delta H_f^\circ_{298}$  values of the methanesulfenic acid in this work. The values show good agreement across the isodesmic reaction series with a standard deviation on the order of  $0.3$  kcal/mol. The average  $\Delta H_f^\circ_{298}$  from isodesmic

**Table 2.3** Reaction Enthalpies at 298K and Calculated Enthalpies of Formation for Methanesulfenic Acid and Its Radicals (kcal/mol)

Isodesmic Reactions	CBS-QB3	
	$\Delta H_{\text{rxn}}^{\circ}$	$\Delta H_{\text{f} 298}^{\circ}$
$\text{CH}_3\text{SOH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3\text{SH}$	45.19	-34.37
$\text{CH}_3\text{SOH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{SH} + \text{CH}_3\text{CH}_2\text{OOH}$	44.98	-34.02
$\text{CH}_3\text{SOH} + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3\text{SCH}_3$	38.21	-34.98
$\text{CH}_3\text{SOH} + \text{CH}_3\text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3\text{CH}_2\text{SCH}_3$	40.95	-35.44
Average value and deviation (reference data)	-34.70±0.48 (-33.34[53], 42.8 [54], -45.45 [48], -33.9 [55])	
$\text{CH}_3\text{SO}\cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{SOH} + \text{CH}_3\text{O}\cdot$	36.93	-19.45
$\text{CH}_3\text{SO}\cdot + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{SCH}_3 + \text{CH}_3\text{OO}\cdot$	56.03	-18.85
$\text{CH}_3\text{SO}\cdot + \text{CH}_4 \rightarrow \text{CH}_3\text{O}\cdot + \text{CH}_3\text{SH}$	34.68	-18.15
$\text{CH}_3\text{SO}\cdot + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{SOH} + \text{CH}_3\text{OO}\cdot$	17.82	-18.57
$\text{CH}_3\text{SO}\cdot + \text{CH}_3\text{CH}_2\text{OOH} \rightarrow \text{CH}_3\text{SOH} + \text{CH}_3\text{CH}_2\text{OO}\cdot$	17.56	-19.30
$\text{CH}_3\text{SO}\cdot + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{SOH} + \text{CH}_3\text{CH}_2\text{O}\cdot$	36.92	-19.40
Average value and deviation (reference data)	-18.95±0.59(-16[15], -16.7[56], -18.8[41])	
$\cdot\text{CH}_2\text{SOH} + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\cdot + \text{CH}_3\text{SOH}$	8.14	6.20
$\cdot\text{CH}_2\text{SOH} + \text{CH}_3\text{OH} \rightarrow \cdot\text{CH}_2\text{OH} + \text{CH}_3\text{SOH}$	3.30	6.10
$\cdot\text{CH}_2\text{SOH} + \text{CH}_3\text{SH} \rightarrow \cdot\text{CH}_2\text{SH} + \text{CH}_3\text{SOH}$	2.04	7.12
$\cdot\text{CH}_2\text{SOH} + \text{CH}_3\text{CH}_2\text{OOH} \rightarrow \cdot\text{CH}_2\text{CH}_2\text{OOH} + \text{CH}_3\text{SOH}$	9.84	6.35
Average value and deviation	6.44±0.30	

**Table 2.4** Reaction Enthalpies at 298K and Calculated Enthalpies of Formation for Ethanesulfenic Acid and Its Radicals (kcal/mol)

Isodesmic Reactions	CBS-QB3	
	$\Delta H_{\text{rxn}}^{\circ}$	$\Delta H_{\text{f}}^{\circ}_{298}$
$\text{CH}_3\text{CH}_2\text{SOH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OOH} + \text{CH}_3\text{SH}$	43.23	-40.31
$\text{CH}_3\text{CH}_2\text{SOH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{CH}_2\text{OOH} + \text{CH}_3\text{SOH}$	-1.96	-40.64
$\text{CH}_3\text{CH}_2\text{SOH} + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_3\text{SOH}$	1.21	-40.18
$\text{CH}_3\text{CH}_2\text{SOH} + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{OOH} + \text{CH}_3\text{SCH}_3$	36.25	-40.92
Average value and deviation		-40.51±0.33
$\text{CH}_3\text{CH}_2\text{SO}\cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OO}\cdot + \text{CH}_3\text{SH}$	59.89	-24.07
$\text{CH}_3\text{CH}_2\text{SO}\cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}\cdot + \text{CH}_3\text{CH}_2\text{SOH}$	36.03	-24.46
$\text{CH}_3\text{CH}_2\text{SO}\cdot + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{OO}\cdot + \text{CH}_3\text{CH}_2\text{SOH}$	16.92	-23.58
$\text{CH}_3\text{CH}_2\text{SO}\cdot + \text{CH}_3\text{CH}_2\text{OOH} \rightarrow \text{CH}_3\text{CH}_2\text{OO}\cdot + \text{CH}_3\text{CH}_2\text{SOH}$	16.66	-24.37
Average value and deviation		-24.12±0.34

**Table 2.4** Reaction Enthalpies at 298K and Calculated Enthalpies of Formation for Ethanesulfenic Acid and Its Radicals (kcal/mol)  
(Continued)

Isodesmic Reactions	CBS-QB3	
	$\Delta H_{\text{rxn}}^{\circ}$	$\Delta H_{\text{f}298}^{\circ}$
$\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{CH}_2\text{OH} + \text{CH}_3\text{SOH}$	-1.14	8.82
$\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{SOH}$	0.61	9.19
$\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH} + \text{CH}_3\text{OOH} \rightarrow \text{C}\cdot\text{H}_2\text{CH}_2\text{OOH} + \text{CH}_3\text{SOH}$	-0.37	9.67
$\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{CH}_2\text{OOH} + \text{CH}_3\text{SH}$	44.82	9.00
Average value and deviation		9.17±0.36
$\text{CH}_3\text{C}\cdot\text{HSOH} + \text{CH}_3\text{OH} \rightarrow \text{C}\cdot\text{H}_2\text{OH} + \text{CH}_3\text{CH}_2\text{SOH}$	3.97	-0.47
$\text{CH}_3\text{C}\cdot\text{HSOH} + \text{CH}_3\text{SH} \rightarrow \text{C}\cdot\text{H}_2\text{SH} + \text{CH}_3\text{CH}_2\text{SOH}$	2.71	-1.56
$\text{CH}_3\text{C}\cdot\text{HSOH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{SOH} + \text{CH}_3\text{C}\cdot\text{HOH}$	2.27	-0.10
$\text{CH}_3\text{C}\cdot\text{HSOH} + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{SOH} + \text{CH}_3\text{C}\cdot\text{HCH}_3$	7.24	-0.71
Average value and deviation (theoretical and experiment data)		-0.71±0.39

reactions are:  $-40.51$ ,  $-24.14$ ,  $9.17$  and  $-0.71$  kcal/mol for  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{CH}_3\text{CH}_2\text{SO}\cdot$ ,  $\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$  and  $\text{CH}_3\text{C}\cdot\text{HSOH}$ , respectively.

**2.3.2.3 Ethenesulfenic Acid ( $\text{CH}_2=\text{CHSOH}$ ) and Its Radicals** The calculated reaction enthalpies and  $\Delta H_f^\circ_{298}$  for the ethenesulfenic acid and its radicals calculated over isodesmic working reaction are tabulated in Table 2.5. The value obtained for the heat of formation of the  $\text{CH}_3\text{SOH}$  and  $\text{CH}_3\text{CH}_2\text{SOH}$  is used to calculate the heat of formation of  $\text{CH}_2=\text{CHSOH}$ . The recommended  $\Delta H_f^\circ_{298}$  for it is  $-10.55$ , with a standard deviation of  $0.91$  kcal/mol, compatible with the reference data in the parenthesis.  $\Delta H_f^\circ_{298}$  for  $\text{CH}_2=\text{CHSO}\cdot$  radical is  $4.52\pm 0.65$  kcal/mol at CBS-QB3 calculation level.

**2.3.2.4 Ethenethiol ( $\text{CH}_2=\text{CHSH}$ ) and Its Radicals.** Luo and Holmes [58] gave the value of heat formation for  $\text{CH}_2=\text{CHSH}$  ( $19.8\pm 1$  kcal/mol) using group equivalents, and group additivity method yield a value of  $20.9$  kcal/mol, which is a little greater than the value of  $18.39\pm 1.92$  kcal/mol calculated in this work.

Gregory and Jenks obtained the  $\Delta H_f^\circ_{298}$  for  $\text{CH}_2=\text{CHS}\cdot$  of the value of  $46.4$  kcal/mol under G2 (MP2, SVP) calculation level, which is similar to the result of  $46.08\pm 0.51$  kcal/mol in this work. The values are listed in Table 2.6.

**Table 2.5** Reaction Enthalpies at 298K and Calculated Enthalpies of Formation for Ethenesulfenic Acid and Its Radicals (kcal/mol)

Isodesmic Reactions	CBS-QB3	
	$\Delta H_{\text{rxn}}^{\circ}$	$\Delta H_{\text{f}298}^{\circ}$
$\text{CH}_2=\text{CHSOH} + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_3 + \text{CH}_3\text{SOH}$	0.57	-9.65
$\text{CH}_2=\text{CHSOH} + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_3 + \text{CH}_3\text{CH}_2\text{SOH}$	-0.63	-10.15
$\text{CH}_2=\text{CHSOH} + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{CH}_3\text{SOH}$	0.81	-10.64
$\text{CH}_2=\text{CHSOH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{CHOH} + \text{CH}_3\text{SOH}$	-4.91	-11.77
Average value and deviation (reference data)	-10.55±0.91(-10.9 [41], -11.8 [41])	
$\text{CH}_2=\text{CHSO}\cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{CHCH}_3 + \text{CH}_3\text{SO}\cdot$	1.21	4.98
$\text{CH}_2=\text{CHSO}\cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{CHSOH} + \text{CH}_3\text{O}\cdot$	37.57	4.06
Average value and deviation (reference data)	4.52±0.65 (6.3 [41])	

**Table 2.6** Reaction Enthalpies at 298K and Calculated Enthalpies of Formation for Ethenethiol and Its radicals (kcal/mol)

Isodesmic Reactions	CBS-QB3	
	$\Delta H_{\text{rxn}}^{\circ}$	$\Delta H_f^{\circ}_{298}$
$\text{CH}_2=\text{CHSH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{CHOH} + \text{CH}_3\text{SH}$	-4.68	16.70
$\text{CH}_2=\text{CHSH} + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_3 + \text{CH}_3\text{SH}$	0.80	18.85
$\text{CH}_2=\text{CHSH} + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_3 + \text{CH}_3\text{CH}_2\text{SH}$	-2.92	21.81
$\text{CH}_2=\text{CHSH} + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{CH}_3\text{SH}$	1.04	18.37
$\text{CH}_2=\text{CHSH} + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_2=\text{CHOH} + \text{CH}_3\text{SCH}_3$	-11.66	16.23
Average value and deviation (reference data)	18.39±1.92 (19.8±1)	
$\text{CH}_2=\text{CHS}\cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{CHO}\cdot + \text{CH}_3\text{SH}$	-0.92	46.04
$\text{CH}_2=\text{CHS}\cdot + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_2=\text{CHCH}_3 + \text{CH}_3\text{S}\cdot$	-7.90	45.43
$\text{CH}_2=\text{CHS}\cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_3 + \text{CH}_3\text{S}\cdot$	8.24	46.68
$\text{CH}_2=\text{CHS}\cdot + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{CH}_3\text{S}\cdot$	8.471	46.20
Average value and deviation (reference data)	46.08±0.51(46.4)	



**Table 2.7** Reaction Enthalpies at 298K and Calculated Enthalpies of Formation for Sulfenic Ester and Its Radicals (kcal/mol)

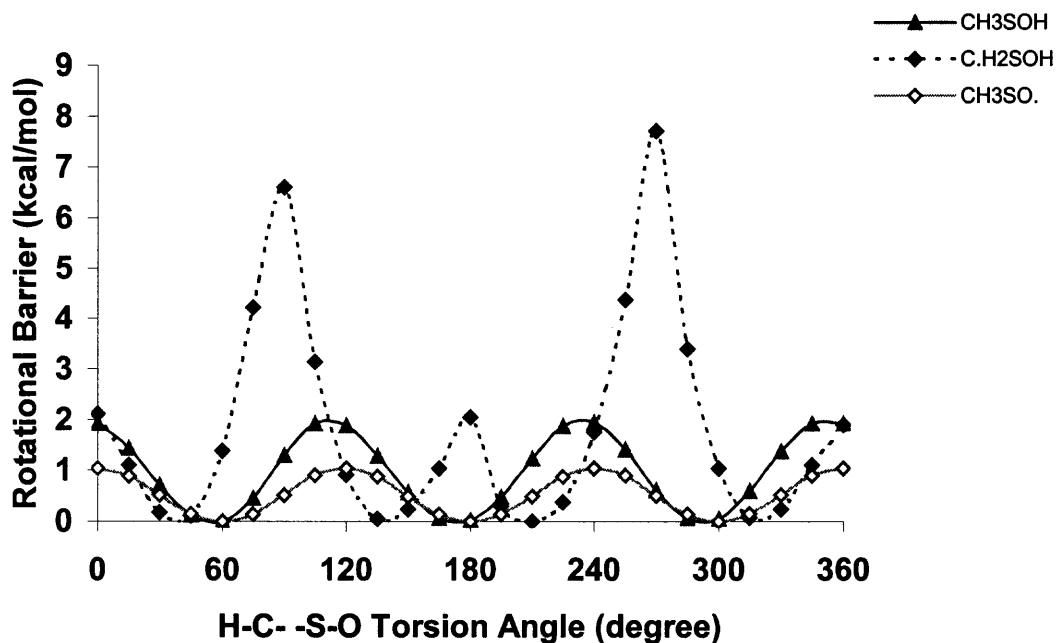
Isodesmic Reactions	CBS-QB3	
	$\Delta H_{\text{rxn}}^{\circ}$	$\Delta H_{\text{f}298}^{\circ}$
$\text{CH}_2=\text{CHOSH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{CHOOH} + \text{CH}_3\text{SH}$	35.18	-2.19
$\text{CH}_2=\text{CHOSH} + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_2=\text{CHOOH} + \text{CH}_3\text{SCH}_3$	28.20	-2.80
$\text{CH}_2=\text{CHOSH} + \text{CH}_3\text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_2=\text{CHOOH} + \text{CH}_3\text{CH}_2\text{SCH}_3$	30.94	-3.26
Average value and deviation(reference data)	-2.75±0.54 (-3.8)	
$\text{CH}_2=\text{CHOS}\cdot + \text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{CHOSH} + \text{CH}_3\text{O}\cdot$	27.91	21.52
$\text{CH}_2=\text{CHOS}\cdot + \text{CH}_3\text{OOH} \rightarrow \text{CH}_2=\text{CHOSH} + \text{CH}_3\text{OO}\cdot$	8.80	22.40
Average value and deviation (reference data)	21.96±0.62 (23.7)	

**2.3.2.5 Sulfenic Ester and Its Radicals.** Sulfenic ester,  $\text{CH}_2=\text{CHOSH}$ , is studied in this work, giving the estimated heat of formation, is  $-2.75$  kcal/mol. The value of  $\Delta H_f^\circ$  for the radical is  $21.96$  kcal/mol, smaller than the value of  $23.7$  kcal/mol obtained by Gregory. The values are listed in Table 2.7.

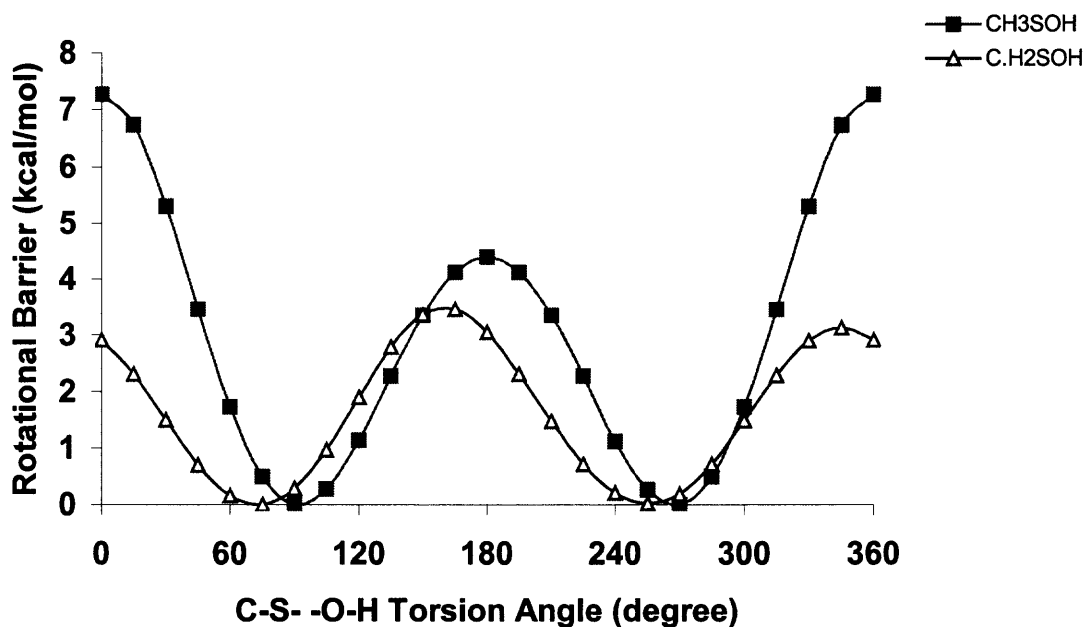
### 2.3.3 Rotational Barrier

Potential barrier for internal rotations of all the species are calculated at the B3LYP/6-311g(d,p) level. Potential energy as function of dihedral angle is determined by varying the torsional angle from  $0^\circ$  to  $360^\circ$  at  $15^\circ$  intervals and allowing the remaining structure parameters to be optimized. Each minimum and maximum on the torsional structures is fully optimized.

**2.3.3.1 Methanesulfenic Acid and Its Radicals** Figure 2.2 shows the rotational barriers about C—S bond. The curves for C-S torsional potential of  $\text{CH}_3\text{SOH}$ , and  $\text{CH}_3\text{SO}\cdot$  are symmetric and show three-fold symmetry with barriers  $1.90$  and  $1.04$  kcal/mol. The barrier for stable parent is higher than that of the corresponding radical due to reduced steric effect by the loss of hydroxyl H atom. The stable conformers for  $\text{C}\cdot\text{H}_2\text{SOH}$  occur when  $\angle\text{H-C--S-O}=45^\circ$ , which allows an interaction between the O atom and the H atom in the  $-\text{C}\cdot\text{H}_2$  group, showing the potential barrier  $7.71$  kcal/mol. The distance between the O and H atoms is  $2.89\text{\AA}$  at this dihedral.



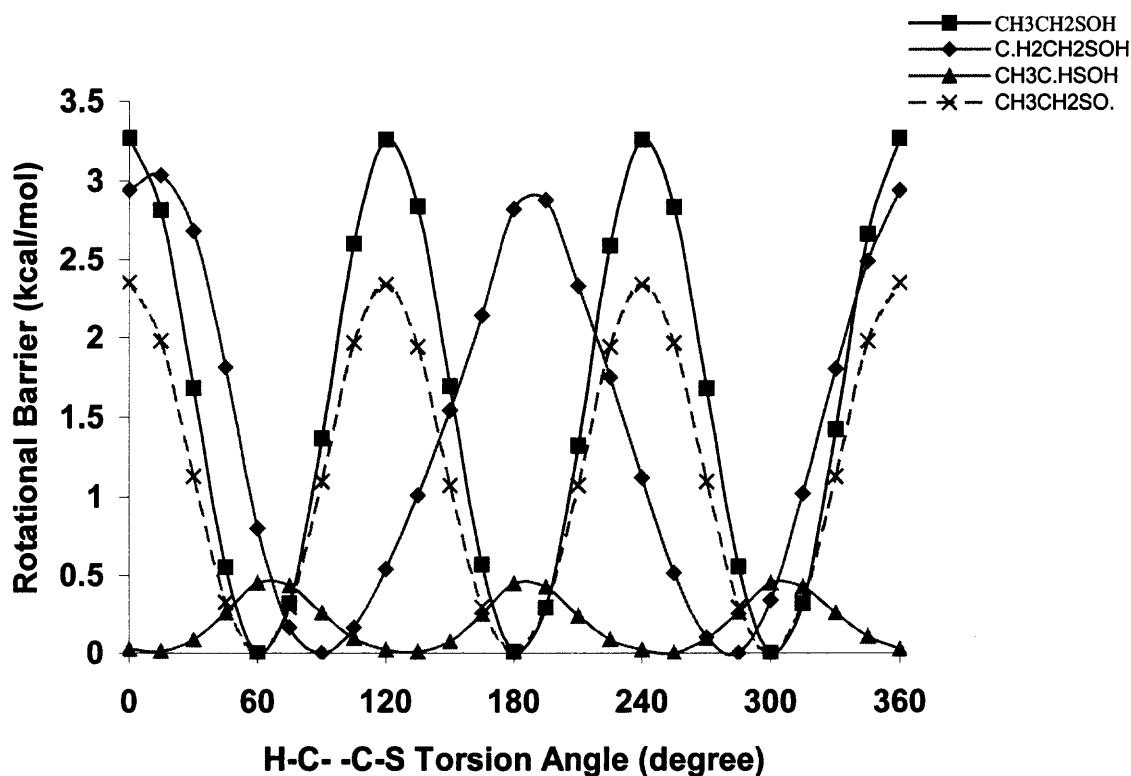
**Figure 2.2** Potential barrier for internal rotation about the C—S bond of  $\text{CH}_3\text{SOH}$ ,  $\text{CH}_3\text{SO}\cdot$ , and  $\text{C}\cdot\text{H}_2\text{SOH}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.



**Figure 2.3** Potential barrier for internal rotation about the S—O bond of  $\text{CH}_3\text{SOH}$  and  $\text{C}\cdot\text{H}_2\text{SOH}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.

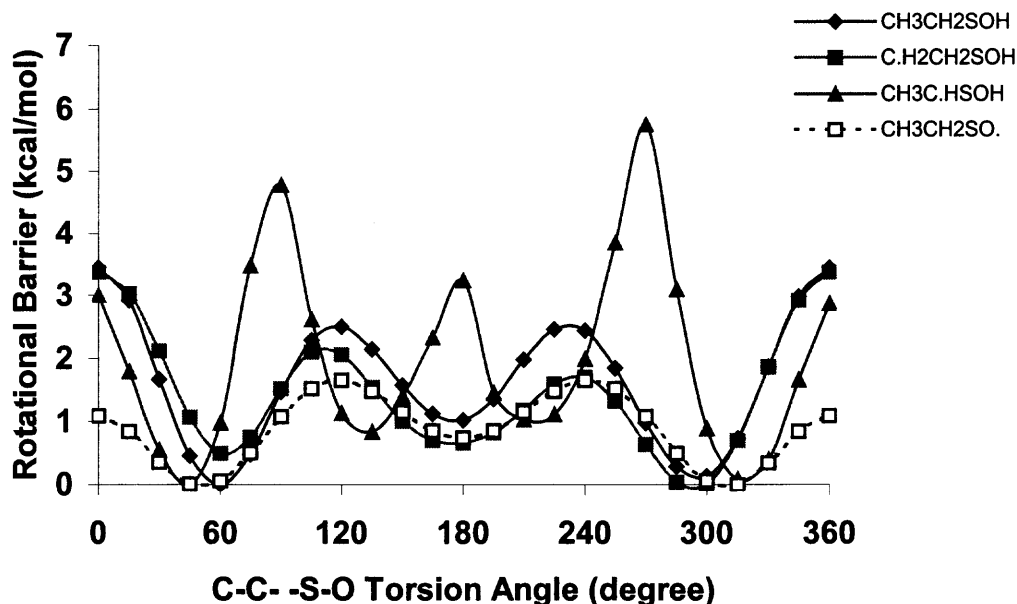
Figure 2.3 shows the rotational barriers about CS—OH bond for  $\text{CH}_3\text{SOH}$  and  $\text{C}\cdot\text{H}_2\text{SOH}$ . The conformers with dihedral  $\angle\text{H-C--C-S}=90^\circ$  are most stable for  $\text{CH}_3\text{SOH}$ ; and the conformers with  $\angle\text{C-S--O-H}=75^\circ$  are stable for  $\text{C}\cdot\text{H}_2\text{SOH}$ .

**2.3.3.2 Ethanesulfenic acid and its radicals.** The calculated rotational barriers about the C—C bond of  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{CH}_3\text{CH}_2\text{SO}\cdot$ ,  $\text{C}\cdot\text{H}_2\text{CH}_2\text{OOH}$  and  $\text{CH}_3\text{C}\cdot\text{HSOH}$  are shown in Figure 2.4.  $\text{CH}_3\text{CH}_2\text{SOH}$ , and  $\text{CH}_3\text{CH}_2\text{SO}\cdot$  have three minima and three maxima representing typical  $\text{CH}_3\text{—C}$  bond rotational potentials, with the potential barrier 3.26kcal/mol and 2.34kcal/mol, respectively, which are in a range common to methyl group rotations.



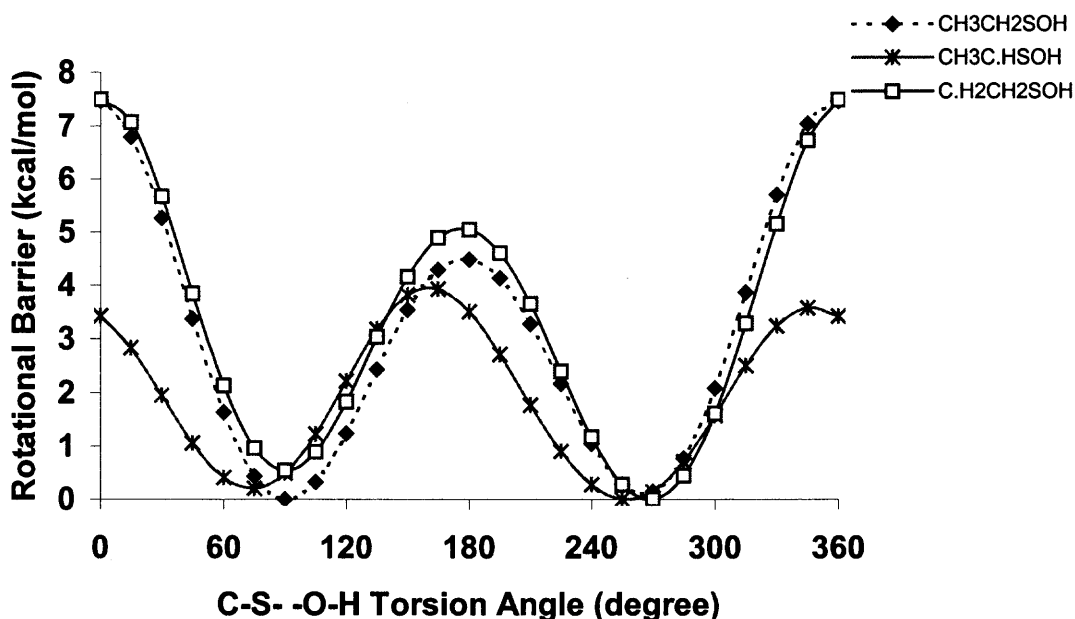
**Figure 2.4** Potential barrier for internal rotation about the C—C bond of  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{CH}_3\text{CH}_2\text{SO}\cdot$ ,  $\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$  and  $\text{CH}_3\text{C}\cdot\text{HSOH}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.

The most stable conformer for  $\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$  has the dihedral  $\angle\text{H}\text{-C}\text{-}\text{C}\text{-}\text{S}\approx 90^\circ$  or  $285^\circ$ , at the potential barrier 3.04 kcal/mol.  $\text{CH}_3\text{C}\cdot\text{HSOH}$  has three  $\text{H}\text{-SOH}$  eclipsed conformers with barriers 0.45kcal/mol.



**Figure 2.5** Potential barrier for internal rotation about the C—S bond of  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{CH}_3\text{CH}_2\text{SO}\cdot$ ,  $\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$  and  $\text{CH}_3\text{C}\cdot\text{HSOH}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.

The calculated rotational barriers about the C—S bond of  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{CH}_3\text{CH}_2\text{SO}\cdot$ ,  $\text{C}\cdot\text{H}_2\text{CH}_2\text{OOH}$  and  $\text{CH}_3\text{C}\cdot\text{HSOH}$  are shown in Figure 2.5. There are three conformers in  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{CH}_3\text{CH}_2\text{SO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$ ; two are  $\text{CH}_3\text{-O}$  gauche conformers, and one in  $\text{CH}_3\text{-O}$  anti conformer. The difference between the  $\text{CH}_3\text{-O}$  anti conformer and the  $\text{CH}_3\text{-O}$  gauche conformer is 1.03, 0.66 and 0.74kcal/mol for  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{CH}_3\text{CH}_2\text{SO}\cdot$  and  $\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$ , respectively. The most stable conformer for  $\text{CH}_3\text{C}\cdot\text{HSOH}$  has the dihedral  $\angle\text{C}\text{-C}\text{-}\text{S}\text{-}\text{O}\approx 45^\circ$  or  $330^\circ$ .

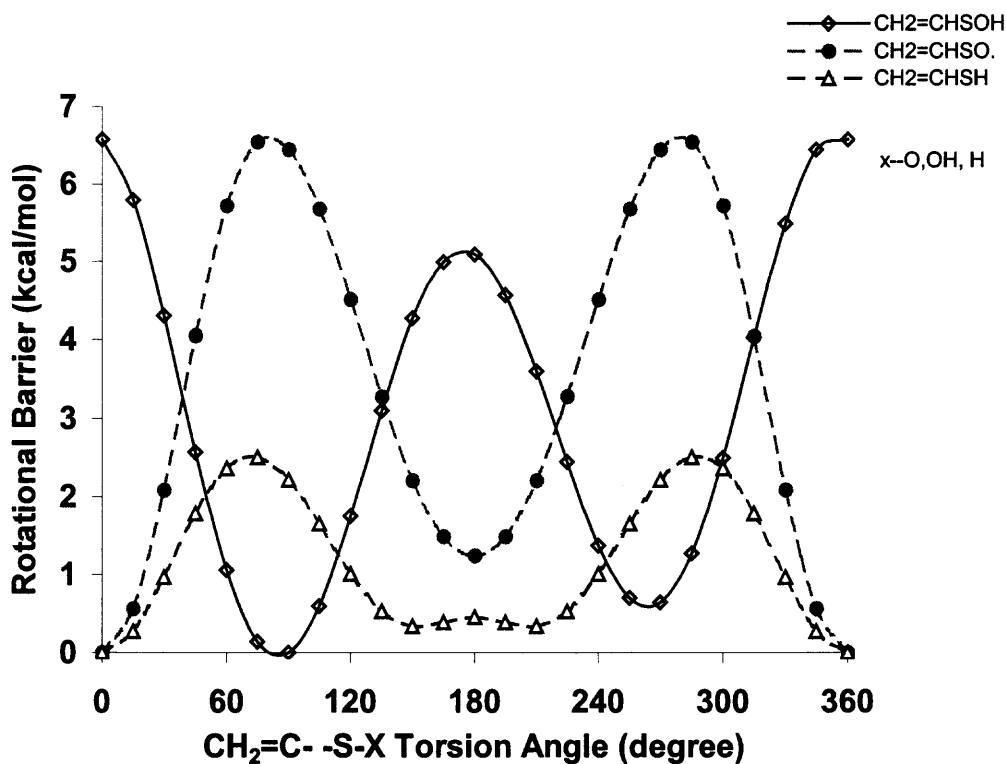


**Figure 2.6** Potential barrier for internal rotation about the S—O bond of  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$  and  $\text{CH}_3\text{C}\cdot\text{HSOH}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.

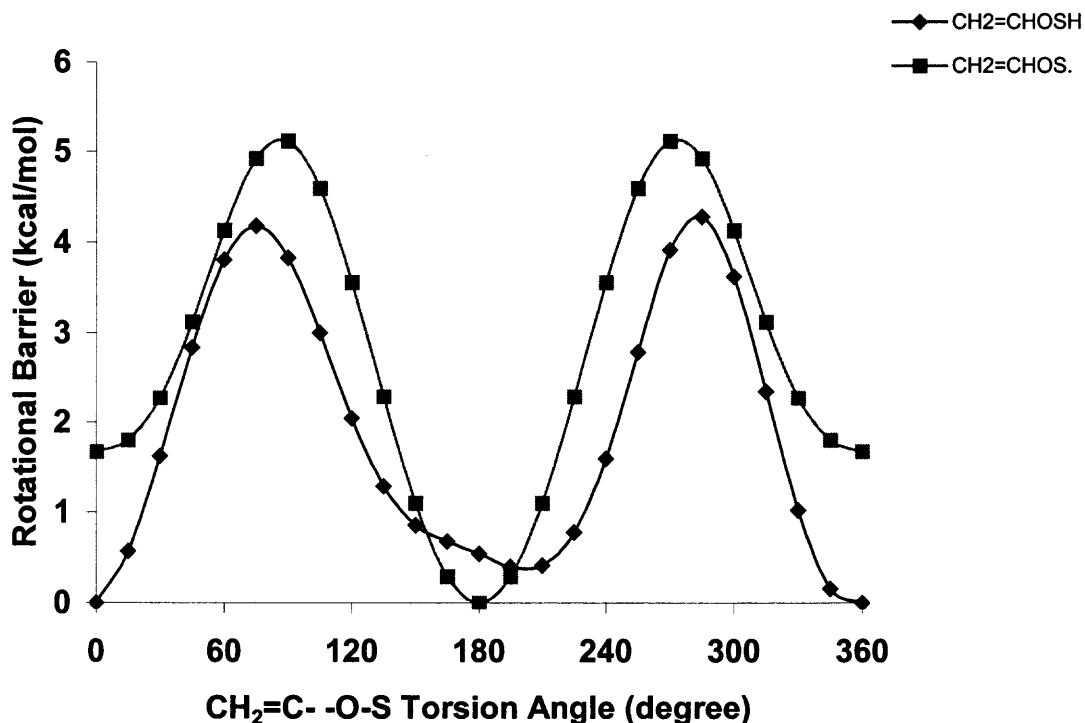
The three curves for  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$  and  $\text{CH}_3\text{C}\cdot\text{HSOH}$  show 2-fold symmetry. The stable structures appear when C-S bond is perpendicular to the O—H bond. The potential barriers about S—O bond are 7.51, 7.49 and 3.9kcal/mol for  $\text{CH}_3\text{CH}_2\text{SOH}$ ,  $\text{C}\cdot\text{H}_2\text{CH}_2\text{SOH}$  and  $\text{CH}_3\text{C}\cdot\text{HSOH}$ . The barriers in the 7kcal/mol range are common in peroxides and hydroperoxides.

**2.3.3.3 Ethenesulfenic Acid, Ethenethiol, Sulfenic Ester and Their Radicals.** The calculated rotational barriers about the C—S bond of  $\text{CH}_2=\text{CHSOH}$ ,  $\text{CH}_2=\text{CHSO}\cdot$ , and  $\text{CH}_2=\text{CHSH}$  are shown in Figure 2.7. For  $\text{CH}_2=\text{CHSOH}$ , due to the interaction between the H atom in the methylene and the hydroxyl H atom, there are 0.64kcal/mol energy difference between the two conformers. The most stable conformer for  $\text{CH}_2=\text{CHSO}\cdot$  is the planar structure ( $\text{CH}_2$  group eclipsed with the O atom) because of electrostatic

reactions; the O··H interaction between H atom in the CH<sub>2</sub> group and the O atom. The minimum on the potential curve of CH<sub>2</sub>=CHSH correspond to the structure in which the H atom in the thiohydroxyl is anti to beta H atom which is 0.34kcal/mol lower than the gauche structure.



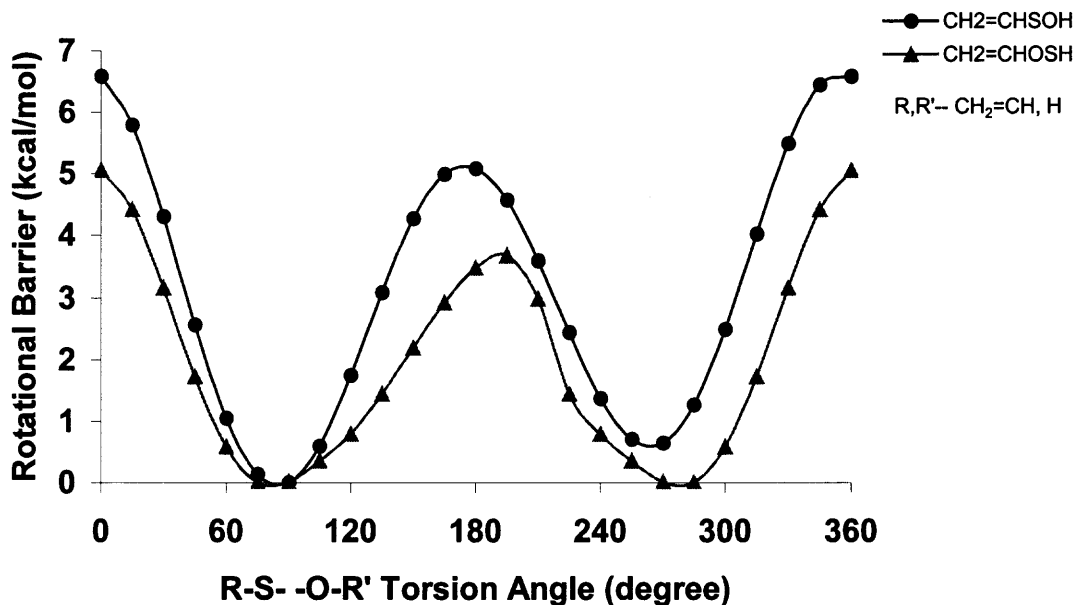
**Figure 2.7** Potential barrier for internal rotation about the C—S bond of CH<sub>2</sub>=CHSOH, CH<sub>2</sub>=CHSO· and CH<sub>2</sub>=CHSH. Points are calculated value at the B3LYP/6-311G(d,p) level.



**Figure 2.8** Potential barrier for internal rotation about the C—O bond of  $\text{CH}_2=\text{CHOSH}$ , and  $\text{CH}_2=\text{CHOS}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.

Figure 2.8 Shows the twofold rotational barriers about the C—O bond for  $\text{CH}_2=\text{CHOSH}$ , and  $\text{CH}_2=\text{CHOS}$ . The  $=\text{CH}_2\text{—S}$  eclipsed conformer of  $\text{CH}_2=\text{CHOSH}$  has the lowest energy because of the interaction between the H atom in the  $\text{CH}_2$  group and the S atom. There are 1.82kcal/mol energy difference between the two conformers in the  $\text{CH}_2=\text{CHOS}$ .





**Figure 2.9** Potential barrier for internal rotation about the S—O bond of  $\text{CH}_2=\text{CHSOH}$  and  $\text{CH}_2=\text{CHOSH}$ . Points are calculated value at the B3LYP/6-311G(d,p) level.

Figure 2.9 shows the calculated potential curve for rotational barriers about the S—O bond in  $\text{CH}_2=\text{CHSOH}$  and  $\text{CH}_2=\text{CHOSH}$ , with the rotational barrier 6.76 and 5.01 kcal/mol. The conformers with dihedral angle  $\angle\text{R-S--O-R}' \approx 90^\circ$  or  $270^\circ$  are most stable because of the electrostatic interactions.

### 2.3.4 Bond Energies

Bond dissociation energies obtained by the CBS-QB3 method are shown in Table 2.8. The O-H BDE is quite similar in three sulfenic acids. And S-O BDE drops about 2 kcal/mol for vinyl group substitutes the alkyl group. The C—S bond weakening of 13 kcal/mol for the ethenesulfenic acid is observed because of  $\text{sp}^2$  hybrid resonance.

**Table 2.8** Bond Dissociation Energies

Reaction series	Bond energy (kcal/mol)
$\text{CH}_3\text{SO—H} \rightarrow \text{CH}_3\text{SO} + \text{H}$	67.85 (69)
$\text{CH}_3\text{CH}_2\text{SO—H} \rightarrow \text{CH}_3\text{CH}_2\text{SO} + \text{H}$	68.49
$\text{CH}_2=\text{CHSO—H} \rightarrow \text{CH}_2=\text{CHSO} + \text{H}$	67.17 (68)
$\text{CH}_3\text{S—OH} \rightarrow \text{CH}_3\text{S} + \text{OH}$	73.39 (73)
$\text{CH}_3\text{CH}_2\text{S—OH} \rightarrow \text{CH}_3\text{CH}_2\text{S} + \text{OH}$	73.5
$\text{CH}_2=\text{CHS—OH} \rightarrow \text{CH}_2=\text{CHS} + \text{OH}$	65.84 (67)
$\text{H—CH}_2\text{SOH} \rightarrow \text{CH}_2\text{SOH} + \text{H}$	93.24
$\text{H—CH}_2\text{CH}_2\text{SOH} \rightarrow \text{CH}_2\text{CH}_2\text{SOH} + \text{H}$	101.78
$\text{CH}_3\text{—SOH} \rightarrow \text{CH}_3 + \text{SOH}$	69.2 (68)
$\text{CH}_3\text{CH}_2\text{—SOH} \rightarrow \text{CH}_3\text{CH}_2 + \text{SOH}$	68.41
$\text{CH}_2=\text{CH—SOH} \rightarrow \text{CH}_2=\text{CH} + \text{SOH}$	81.65
$\text{CH}_3\text{—CH}_2\text{SOH} \rightarrow \text{CH}_3 + \text{CH}_2\text{SOH}$	81.95
$\text{CH}_3\text{C(—H)H SOH} \rightarrow \text{CH}_3\text{CHSOH} + \text{H}$	91.9
$\text{CH}_2=\text{CHS—H} \rightarrow \text{CH}_2=\text{CHS} + \text{H}$	79.79
$\text{CH}_2=\text{CHOS—H} \rightarrow \text{CH}_2=\text{CHOS} + \text{H}$	76.81

Literature data in parenthesis [41]

### 2.3.5 Entropy $S^\circ_{298}$ and Heat Capacity $C_p(T)$ ( $300 \leq T/K \leq 1500$ )

Standard entropy ( $S^\circ_{298}$ ) and heat capacities ( $C_p(T)$ ),  $300 \leq T/K \leq 1500$  are determined from translation, vibration and external rotation are calculated using the “SMCPS” program [58]. This program utilizes the rigid-rotor-harmonic-oscillator approximation from the frequencies along with moments of inertia on the basis of the optimized B3LYP/6-311G(d,p) structures. Contributions to entropy and heat capacity from internal rotations are determined using direct integration over energy levels of the intramolecular rotation potential energy. The results are summarized in Table 2.9.

**Table 2.9** Ideal Gas- Phase Thermodynamic Properties<sup>a</sup>

Species and symmetry #		$\Delta H_f^\circ$ <sup>b</sup>	$S^\circ$ <sup>c</sup>	$C_{p(300)}^\circ$	$C_{p(400)}^\circ$	$C_{p(500)}^\circ$	$C_{p(600)}^\circ$	$C_{p(800)}^\circ$	$C_{p(1000)}^\circ$	$C_{p(1500)}^\circ$
CH <sub>3</sub> SOH (3)	TVR <sup>dh</sup>		61.36	12.41	15.04	17.33	19.22	22.17	24.41	28.08
	I.R. <sup>e</sup>		4.90	2.02	1.81	1.61	1.47	1.30	1.20	1.09
	I.R. <sup>f</sup>		2.25	1.50	1.80	1.99	2.13	2.23	2.18	1.86
	total	-34.70±0.48	68.51	15.93	18.65	20.93	22.82	25.7	27.79	31.03
CH <sub>3</sub> SO· (3)	TVR <sup>dih</sup>		62.50	12.15	14.42	16.41	18.06	20.63	22.53	25.53
	I.R. <sup>e</sup>		5.38	1.51	1.34	1.23	1.16	1.09	1.06	1.02
	total	-18.95±0.59	69.24 <sup>i</sup>	13.66	15.76	17.64	19.22	21.72	23.59	26.55
C·H <sub>2</sub> SOH (2)	TVR <sup>dih</sup>		63.63	12.97	15.12	16.75	18.00	19.85	21.26	23.70
	I.R. <sup>e</sup>		2.75	1.75	1.95	2.09	2.19	2.29	2.24	1.94
	I.R. <sup>f</sup>		2.97	1.99	2.12	2.08	1.97	1.72	1.54	1.28
	total	6.44±0.30	69.35 <sup>i</sup>	16.71	19.19	20.92	22.16	23.86	25.04	26.92
CH <sub>3</sub> CH <sub>2</sub> SOH (3)	TVR <sup>dh</sup>		63.90	15.31	19.51	23.27	26.43	31.37	35.06	40.95
	I.R. <sup>g</sup>		4.28	2.13	2.19	2.09	1.95	1.69	1.50	1.26
	I.R. <sup>e</sup>		5.91	2.28	2.30	2.20	2.05	1.76	1.56	1.29
	I.R. <sup>f</sup>		2.24	1.49	1.78	1.99	2.12	2.23	2.19	1.89
	total	-40.51±0.33	76.33	21.21	25.78	29.55	32.55	37.05	40.31	45.39
CH <sub>3</sub> CH <sub>2</sub> SO· (3)	TVR <sup>dih</sup>		63.74	13.31	17.00	20.40	23.30	27.83	31.19	36.41
	I.R. <sup>g</sup>		4.69	2.13	1.99	1.80	1.64	1.42	1.29	1.14
	I.R. <sup>e</sup>		6.71	2.00	1.73	1.53	1.40	1.24	1.16	1.07
	total	-24.12±0.34	76.51 <sup>i</sup>	17.44	20.72	23.73	26.34	30.49	33.64	38.62
C·H <sub>2</sub> CH <sub>2</sub> SOH (3)	TVR <sup>dih</sup>		66.54	16.02	19.77	22.87	25.37	29.16	31.99	36.60
	I.R. <sup>g</sup>		3.79	2.19	2.18	2.05	1.89	1.63	1.45	1.23
	I.R. <sup>e</sup>		5.89	2.29	2.29	2.18	2.03	1.75	1.54	1.28
	I.R. <sup>f</sup>		2.24	1.49	1.78	1.98	2.12	2.23	2.19	1.89
	total	9.17±0.36	79.84 <sup>i</sup>	21.99	26.02	29.08	31.41	34.77	37.17	41.00
CH <sub>3</sub> C·HSOH (3)	TVR <sup>dih</sup>		66.97	15.63	19.25	22.36	24.92	28.87	31.83	36.58
	I.R. <sup>g</sup>		5.65	1.11	1.06	1.04	1.03	1.01	1.01	1.00
	I.R. <sup>e</sup>		5.16	2.09	2.22	2.29	2.32	2.23	2.05	1.66
	I.R. <sup>f</sup>		2.85	1.93	2.12	2.14	2.07	1.85	1.65	1.35
	total	-0.71±0.39	82.01 <sup>i</sup>	20.76	24.65	27.83	30.34	33.96	36.54	40.59

**Table 2.9** Ideal Gas- Phase Thermodynamic Properties.<sup>a</sup> (Continued)

Species and symmetry #		$\Delta H_f^\circ$ <sup>b</sup>	$S^\circ$ <sup>c</sup>	$C_{p(300)}$ <sup>c</sup>	$C_{p(400)}$ <sup>c</sup>	$C_{p(500)}$ <sup>c</sup>	$C_{p(600)}$ <sup>c</sup>	$C_{p(800)}$ <sup>c</sup>	$C_{p(1000)}$ <sup>c</sup>	$C_{p(1500)}$ <sup>c</sup>
CH <sub>2</sub> =CHSH (2)	TVR <sup>dh</sup>		62.03	13.36	16.32	18.83	20.89	24.11	26.51	30.31
	I.R. <sup>e</sup>		3.97	2.18	2.05	1.87	1.70	1.47	1.33	1.15
	total	18.39±1.92	66.00	15.54	18.37	20.7	22.59	25.58	27.84	31.46
CH <sub>2</sub> =CHSOH (2)	TVR <sup>dh</sup>		65.56	15.20	18.72	21.59	23.87	27.26	29.73	33.68
	I.R. <sup>e</sup>		5.18	2.19	2.31	2.33	2.28	2.08	1.86	1.49
	I.R. <sup>f</sup>		2.34	1.58	1.87	2.06	2.16	2.21	2.11	1.76
	total	-10.55±0.91	73.08	18.97	22.90	25.98	28.31	31.55	33.7	36.93
CH <sub>2</sub> =CHOSH (2)	TVR <sup>dh</sup>		65.38	14.94	18.45	21.39	23.77	27.39	30.02	34.07
	I.R. <sup>l</sup>		5.46	2.24	2.32	2.30	2.22	1.96	1.74	1.40
	I.R. <sup>f</sup>		3.17	1.96	2.16	2.25	2.25	2.11	1.91	1.54
	total	-2.75±0.54	74.01	19.14	22.93	25.94	28.24	31.46	33.67	37.01
CH <sub>2</sub> =CHS· (2)	TVR <sup>dih</sup>		61.68	13.05	15.67	17.87	19.66	22.35	24.31	27.38
	I.R. <sup>e</sup>		0	0	0	0	0	0	0	0
	total	46.08±0.51	63.06 <sup>i</sup>	13.05	15.67	17.87	19.66	22.35	24.31	27.38
CH <sub>2</sub> =CHSO· (2)	TVR <sup>dih</sup>		67.30	15.16	18.23	20.76	22.78	25.76	27.88	31.15
	I.R. <sup>e</sup>		4.71	2.08	2.18	2.27	2.32	2.30	2.17	1.78
	total	4.52±0.65	73.39 <sup>i</sup>	17.24	20.41	23.03	25.10	28.08	30.05	32.93
CH <sub>2</sub> =CHOS· (2)	TVR <sup>dih</sup>		66.27	14.45	17.60	20.22	22.32	25.43	27.63	31.00
	I.R. <sup>l</sup>		5.26	2.16	2.28	2.33	2.31	2.15	1.94	1.55
	total	21.96±0.62	72.91 <sup>i</sup>	16.61	19.88	22.55	24.63	27.58	29.57	32.55

<sup>a</sup> Thermodynamic properties are referred to standard state of an ideal gas of pure enantiomer at 1 atm.

The torsional frequencies are excluded in the calculation of entropies and heat capacities. Instead, a more exact contribution from hindered rotations about the C—S, S—O bonds are calculated.

<sup>b</sup> Units in kcal/mol. <sup>c</sup> Units in cal/(mol K). <sup>d</sup> The sum of contributions from translations, external rotations, and vibrations.

<sup>e</sup> Contribution from internal rotation about the C—S bond. <sup>f</sup> Contribution from internal rotation about the S—O bond. <sup>g</sup> Contribution from internal rotation about the C—C bond. <sup>h</sup> Symmetry number is taken into account ( $-1.987\ln(\text{symmetry number})$ ). <sup>i</sup> Spin degeneracy contribution for entropy =  $1.987\ln(2)$  is taken into account. <sup>l</sup> Contribution from internal rotation about the C—O bond.

## 2.4 Summary

Thermodynamic properties of methanesulfenic acid, ethanesulfenic acid, ethenesulfenic acid, ethenethiol, sulfenic ester and corresponding radicals derived from H atom loss parent molecules are calculated using CBS-QB3 method with several isodesmic reaction schemes.  $\Delta H_f^\circ_{298}$  determined over varied isodesmic reaction show good precision.  $S^\circ_{298}$  and  $C_p(T)(300 \leq T/K \leq 1500)$  are determined with B3LYP/6-311G(d,p) optimized geometries and frequencies, hindered internal rotational contributions to  $S^\circ_{298}$  and  $C_p$  are also considered.

## APPENDIX A

### THERMOCHEMICAL CALCULATION RESULTS

Total energies, ZPVE's and Thermal Corrections and  $\Delta H_f^\circ_{298}$  for the standard species used in the working reactions are listed in Table A.1. and Table A.2.

**Table A.1** Total Energies Standard Compounds at 298K

Species	B3LYP/ 6-311g(d,p)	ZPVE	Therm. Corr.	CBS-QB3	ZPVE	Therm. Corr.
CH <sub>4</sub>	-40.48619662	27.44	2.39	-40.4061759	27.71	2.39
C <sub>2</sub> H <sub>6</sub>	-79.77888387	45.77	2.78	-79.6261347	46.21	2.78
C <sub>3</sub> H <sub>8</sub>	-119.0742063	63.37	3.44	-118.8503724	63.98	3.44
CH <sub>3</sub> SCH <sub>3</sub>	-477.9860076	46.42	3.68	-477.3706417	46.82	3.67
CH <sub>3</sub> SCH <sub>2</sub> CH <sub>3</sub>	-517.2817659	64.04	4.49	-516.5957527	64.62	4.49
C·H <sub>2</sub> OH	-115.0547796	22.93	2.68	-114.8838669	23.15	2.68
CH <sub>3</sub> CH <sub>2</sub> OOH	-230.1528196	51.00	4.10	-229.8188427	51.49	4.10
CH <sub>3</sub> OOH	-190.8519933	33.47	3.34	-190.5895531	33.79	3.34
CH <sub>3</sub> OO·	-190.2250891	26.33	3.00	-189.9547064	26.59	3.00
CH <sub>3</sub> CH <sub>2</sub> OO·	-229.5264038	43.82	3.76	-229.1844081	44.24	3.76
C·H <sub>2</sub> OCH <sub>3</sub>	-154.3398094	40.31	3.37	-154.7469275	40.70	3.37
CH <sub>3</sub> OCH <sub>3</sub>	-154.9888967	48.78	3.31	-154.7469275	49.25	3.31

**Table A.2**  $\Delta H_f^\circ_{298}$  for Species in Working Reactions

Speceies	$\Delta H_f^\circ_{298}$ (kcal/mol)	Speceies	$\Delta H_f^\circ_{298}$ (kcal/mol)
CH <sub>4</sub>	-17.89±0.07	CH <sub>3</sub> CH <sub>2</sub> OOH	-39.7±0.3
C <sub>2</sub> H <sub>6</sub>	-20.04± 0.12	CH <sub>3</sub> OOH	-31.8±0.94
C <sub>3</sub> H <sub>8</sub>	-25.02±0.12	CH <sub>3</sub> OO·	2.15±1.22
CH <sub>3</sub> SCH <sub>3</sub>	-8.96±0.48	CH <sub>3</sub> CH <sub>2</sub> OO·	-6.5±2.4
CH <sub>3</sub> SCH <sub>2</sub> CH <sub>3</sub>	-14.42±0.27	CH <sub>3</sub> CH <sub>2</sub> OH	-56.12±0.2
H·	52.10±0.001	OH·	8.89±0.09
CH <sub>3</sub> OH	-48.08±0.05	CH <sub>3</sub> SH	-5.40 ±0.14
CH <sub>3</sub> OCH <sub>3</sub>	-43.99±0.12	CH <sub>3</sub> O·	4.10±1.0
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>3</sub>	-51.73 ± 0.16	CH <sub>3</sub> ·	34.82± 0.2
C <sub>2</sub> H <sub>5</sub> ·	28.80±0.50	CH <sub>3</sub> CH <sub>2</sub> O·	-3.9±1.27
C·H <sub>2</sub> SH	36.3±2	C·H <sub>2</sub> OH	-3.97±0.22
C·H <sub>2</sub> CH <sub>2</sub> OH	-5.70±0.85	C·H <sub>2</sub> CH <sub>2</sub> OOH	11.2±2.1
CH <sub>3</sub> C·HCH <sub>3</sub>	21.0±0.7	·SOH	-0.5±2

**Table A.3** Internal Rotation Contribution to Entropy and Heat Capacity Units: cal/(mol K)

Species		S° <sub>298</sub>	C <sub>p(300)</sub>	C <sub>p(400)</sub>	C <sub>p(500)</sub>	C <sub>p(600)</sub>	C <sub>p(800)</sub>	C <sub>p(1000)</sub>	C <sub>p(1500)</sub> <sup>c</sup>
CH <sub>3</sub> SC·H <sub>2</sub>	CH <sub>3</sub> -SC·H <sub>2</sub>	5.042	1.896	1.663	1.488	1.37	1.224	1.147	1.066
	CH <sub>3</sub> S-C·H <sub>2</sub>	2.955	1.851	2.054	2.187	2.257	2.242	2.106	1.729
CH <sub>3</sub> SCH <sub>2</sub> OOH	CH <sub>3</sub> -SCH <sub>2</sub> OOH	5.461	1.45	1.289	1.193	1.136	1.076	1.049	1.02
	CH <sub>3</sub> S-CH <sub>2</sub> OOH	5.658	2.149	2.258	2.322	2.333	2.21	2.014	1.62
	CH <sub>3</sub> SCH <sub>2</sub> -OOH	5.639	2.162	2.264	2.326	2.335	2.211	2.015	1.621
	CH <sub>3</sub> SCH <sub>2</sub> O-OH	1.885	1.873	2.01	2.106	2.193	2.299	2.309	2.069
CH <sub>3</sub> SCH <sub>2</sub> OO·	CH <sub>3</sub> -SCH <sub>2</sub> OO·	5.248	1.736	1.509	1.364	1.269	1.157	1.102	1.044
	CH <sub>3</sub> S-CH <sub>2</sub> OO·	5.789	2.176	2.285	2.335	2.315	2.148	1.942	1.554
	CH <sub>3</sub> SCH <sub>2</sub> -OO·	6.388	2.308	2.147	1.944	1.761	1.504	1.352	1.166
C·H <sub>2</sub> SCH <sub>2</sub> OOH	C·H <sub>2</sub> SCH <sub>2</sub> OOH	3.098	1.918	2.122	2.23	2.266	2.173	1.989	1.61
	C·H <sub>2</sub> S-CH <sub>2</sub> OOH	5.762	2.215	2.313	2.331	2.265	2.045	1.823	1.461
	C·H <sub>2</sub> SCH <sub>2</sub> -OOH	5.456	2.122	2.208	2.289	2.331	2.3	2.153	1.764
	C·H <sub>2</sub> SCH <sub>2</sub> O-OH	1.817	1.854	1.991	2.086	2.172	2.288	2.317	2.11
TS1	No internal rotor	0	0	0	0	0	0	0	0
TS2	CH <sub>3</sub> - $\overline{\text{SCH}_2\text{OO}}$	5.248	1.736	1.509	1.364	1.269	1.157	1.102	1.044
	CH <sub>3</sub> S- $\overline{\text{CH}_2\text{OO}}$	5.789	2.176	2.285	2.335	2.315	2.148	1.942	1.554
TS3	CH <sub>3</sub> - $\overline{\text{SCH}_2\text{OO}}$	5.248	1.736	1.509	1.364	1.269	1.157	1.102	1.044
TS4	CH <sub>2</sub> S-CH <sub>2</sub> OOH	5.264	1.372	1.221	1.144	1.102	1.057	1.034	1.013
	CH <sub>2</sub> SCH <sub>2</sub> O-OH	3.476	2.233	2.318	2.283	2.174	1.92	1.699	1.377
TS5	$\overline{\text{CH}_2\text{SCH}_2\text{O-OH}}$	1.817	1.854	1.991	2.086	2.172	2.288	2.317	2.11

## Distance matrix (angstroms) For CH3SCH2OOH

		1	2	3	4	5
1	C	0.000000				
2	S	1.832159	0.000000			
3	C	2.826899	1.832937	0.000000		
4	O	3.645867	2.752460	1.409808	0.000000	
5	O	3.364771	3.169152	2.315209	1.450046	0.000000
6	H	3.422334	3.118179	2.751687	1.881681	0.968449
7	H	1.090302	2.383338	3.780005	4.562598	4.240112
8	H	1.090594	2.442723	3.049307	4.081137	3.902450
9	H	1.088403	2.440719	2.986561	3.416293	2.721693
10	H	2.728051	2.421048	1.093090	2.070115	2.533534
11	H	3.708572	2.399324	1.091379	1.971924	3.224452
		6	7	8	9	10
6	H	0.000000				
7	H	4.108672	0.000000			
8	H	4.184419	1.773451	0.000000		
9	H	2.779369	1.780934	1.786718	0.000000	
10	H	3.208561	3.790382	2.601546	2.825599	0.000000
11	H	3.627558	4.583296	3.819439	4.025185	1.791246
		11				
11	H	0.000000				

## Distance matrix (angstroms) For CH3SCH2OO

		1	2	3	4	5
1	C	0.000000				
2	S	1.828035	0.000000			
3	C	2.792511	1.804821	0.000000		
4	O	3.302798	2.721984	1.458290	0.000000	
5	O	3.231695	3.382978	2.299231	1.319871	0.000000
6	H	1.090137	2.374149	3.742679	4.263902	4.238076
7	H	1.090252	2.440265	3.001896	3.694434	3.445465
8	H	1.089034	2.435053	2.970190	2.967568	2.612855
9	H	2.890758	2.439728	1.089575	2.060745	2.352878
10	H	3.750808	2.369308	1.089269	2.036921	3.135961
		6	7	8	9	10
6	H	0.000000				
7	H	1.779528	0.000000			
8	H	1.779189	1.787457	0.000000		
9	H	3.920247	2.694524	3.115955	0.000000	
10	H	4.605441	3.964709	4.005739	1.804837	0.000000



Distance matrix (angstroms) For CH2SCH2OOH

		1	2	3	4	5
1	C	0.000000				
2	S	1.729950	0.000000			
3	C	2.780211	1.841801	0.000000		
4	O	3.527469	2.750613	1.404210	0.000000	
5	O	3.269417	3.219102	2.307901	1.449755	0.000000
6	H	3.207263	3.149131	2.744259	1.887871	0.968792
7	H	1.079847	2.416845	3.793383	4.551679	4.254413
8	H	1.079459	2.462821	2.838338	3.344688	2.722133
9	H	2.750204	2.421486	1.091920	2.070029	2.489290
10	H	3.669066	2.393182	1.091091	1.977793	3.220985
		6	7	8	9	10
6	H	0.000000				
7	H	4.059382	0.000000			
8	H	2.821488	1.886553	0.000000		
9	H	3.149603	3.782601	2.543902	0.000000	
10	H	3.645904	4.598638	3.866937	1.796638	0.000000

Distance matrix (angstroms) For TS1

		1	2	3	4	5
1	C	0.000000				
2	S	1.824708	0.000000			
3	C	2.796504	1.930670	0.000000		
4	H	1.084990	2.498109	3.137693	0.000000	
5	H	1.081761	2.454411	3.736843	1.843816	0.000000
6	H	3.750766	2.470687	1.084191	4.145908	4.617798
7	H	2.970790	2.509904	1.084505	2.918224	4.031183
8	O	3.027132	2.727712	1.428402	3.530442	3.797357
9	O	2.557436	3.186687	2.349452	2.829801	3.281076
10	H	1.484580	2.532507	2.472216	1.943878	2.144796
		6	7	8	9	10
6	H	0.000000				
7	H	1.815000	0.000000			
8	O	2.035757	2.088296	0.000000		
9	O	3.285687	2.482817	1.484274	0.000000	
10	H	3.494855	2.678221	2.041094	1.139966	0.000000

		Distance matrix (angstroms) For TS2				
		1	2	3	4	5
1	C	0.000000				
2	S	1.828454	0.000000			
3	H	1.352374	2.643372	0.000000		
4	H	1.085426	2.466284	1.990183	0.000000	
5	O	1.403389	2.779282	1.880695	2.112806	0.000000
6	O	2.122025	3.475825	1.315731	2.842973	1.610222
7	C	2.840377	1.898506	3.230576	3.834288	2.951342
8	H	2.842845	2.463550	2.773416	3.919725	2.764938
9	H	3.763063	2.430125	4.094031	4.697922	4.025709
10	H	3.148163	2.476348	3.756849	4.083766	2.886244
		6	7	8	9	10
6	O	0.000000				
7	C	3.434852	0.000000			
8	H	2.749119	1.084376	0.000000		
9	H	4.400473	1.084580	1.790139	0.000000	
10	H	3.717751	1.082772	1.781306	1.791598	0.000000

		Distance matrix (angstroms) For TS3				
		1	2	3	4	5
1	C	0.000000				
2	S	1.887544	0.000000			
3	O	2.997004	2.087255	0.000000		
4	C	3.111506	2.288021	2.266644	0.000000	
5	O	3.817115	2.790626	1.666110	1.346173	0.000000
6	H	1.085703	2.438809	2.699623	3.089369	3.559996
7	H	1.085138	2.452197	3.630315	4.118219	4.713319
8	H	1.086884	2.477653	3.789728	3.237183	4.236955
9	H	2.697444	2.618226	2.673171	1.087084	2.094995
10	H	3.833602	2.825556	3.187936	1.084893	2.057762
		6	7	8	9	10
6	H	0.000000				
7	H	1.778442	0.000000			
8	H	1.791346	1.785150	0.000000		
9	H	2.509804	3.777342	2.649405	0.000000	
10	H	4.009783	4.810836	3.755324	1.854358	0.000000

Distance matrix (angstroms) For TS4

		1	2	3	4	5
1	C	0.000000				
2	S	1.657469	0.000000			
3	C	2.835735	2.024299	0.000000		
4	O	3.542783	2.827057	1.301010	0.000000	
5	O	3.006359	3.131156	2.428002	1.811961	0.000000
6	H	3.958760	4.030395	3.013322	2.087818	0.967067
7	H	1.083191	2.386305	3.857776	4.614421	4.004652
8	H	1.083941	2.386444	2.820352	3.294578	2.355224
9	H	2.680921	2.471340	1.098350	2.050710	2.598377
10	H	3.589035	2.423074	1.098715	1.994727	3.472865
		6	7	8	9	10
6	H	0.000000				
7	H	4.950568	0.000000			
8	H	3.231899	1.883644	0.000000		
9	H	3.173431	3.653696	2.451386	0.000000	
10	H	3.975818	4.502377	3.779996	1.829643	0.000000

Distance matrix (angstroms) For TS5

		1	2	3	4	5
1	C	0.000000				
2	S	1.773850	0.000000			
3	C	2.427881	1.837933	0.000000		
4	O	2.000477	2.486673	1.434198	0.000000	
5	O	3.680697	4.009345	2.393221	1.707726	0.000000
6	H	1.082370	2.475167	3.289161	2.614893	4.232737
7	H	1.082543	2.487597	2.826998	2.382886	3.850397
8	H	2.952570	2.468134	1.091996	2.089661	2.658721
9	H	3.342527	2.463703	1.088830	2.095649	2.507679
10	H	3.892762	4.376915	2.987369	2.018048	0.967459
		6	7	8	9	10
6	H	0.000000				
7	H	1.856079	0.000000			
8	H	3.960735	2.968836	0.000000		
9	H	4.051678	3.877682	1.799379	0.000000	
10	H	4.206582	4.198673	3.479392	3.005171	0.000000

## APPENDIX B

### RATE CONSTANTS IN QRRK CALCULATIONS

**Table B.1** Calculated Reaction Parameters at P=0.001 atm,  $k = A(T)^n \exp(-E_a/RT)$   
(T=200-2000K)

Reaction	$A(s^{-1})$	$n$	$E_a$ (kcal/mol)	$k_{298} (s^{-1})$
$CH_3SC \cdot H_2 + O_2 \rightarrow CH_3SCH_2OO \cdot$	6.549E+68	-19.60	10.49	1.845E+12
$CH_3SC \cdot H_2 + O_2 \rightarrow C \cdot H_2SCH_2OOH$	3.282E+66	-19.11	10.64	1.289E+11
$CH_3SC \cdot H_2 + O_2 \rightarrow CH_3SC(=O)H + OH$	4.661E+08	0.73	11.10	2.167E+02
$CH_3SC \cdot H_2 + O_2 \rightarrow CH_3S(=O) + CH_2O$	3.253E+08	0.49	6.05	1.887E+05
$CH_3SC \cdot H_2 + O_2 \rightarrow CH_2S + CH_2O + OH$	2.148E+12	-0.48	5.06	2.231E+07
$CH_3SC \cdot H_2 + O_2 \rightarrow CYCH_2SCH_2O + OH$	2.693E+11	-0.58	11.58	2.759E+01
$CH_3SCH_2OO \cdot \rightarrow CH_3SC \cdot H_2 + O_2$	1.610E-10	5.89	15.93	1.613E-06
$CH_3SCH_2OO \cdot \rightarrow CH_3SC(=O)H + OH$	2.522E-41	12.65	20.83	6.610E-24
$CH_3SCH_2OO \cdot \rightarrow C \cdot H_2SCH_2OOH$	1.139E+04	1.55	14.62	3.445E-03
$CH_3SCH_2OO \cdot \rightarrow CH_3S(=O) + CH_2O$	1.760E-39	12.85	15.34	1.700E-17
$C \cdot H_2SCH_2OOH \rightarrow CH_3SCH_2OO \cdot$	1.052E-08	5.13	4.70	1.003E+02
$C \cdot H_2SCH_2OOH \rightarrow CH_2S + CH_2O + OH$	5.108E-76	25.31	-2.66	1.654E-09
$C \cdot H_2SCH_2OOH \rightarrow CYCH_2SCH_2O + OH$	5.683-116	36.63	-5.76	1.353E-18

**Table B.2** Calculated Reaction Parameters at P=0.01 atm,  $k = A(T)^n \exp(-E_a/RT)$   
(T=200-2000K)

Reaction	$A(s^{-1})$	$n$	$E_a$ (kcal/mol)	$k_{298} (s^{-1})$
$CH_3SC \cdot H_2 + O_2 \rightarrow CH_3SCH_2OO \cdot$	6.396E+68	-19.24	11.19	3.766E+12
$CH_3SC \cdot H_2 + O_2 \rightarrow C \cdot H_2SCH_2OOH$	1.665E+69	-19.60	12.37	1.901E+11
$CH_3SC \cdot H_2 + O_2 \rightarrow CH_3SC(=O)H + OH$	4.668E+08	0.73	11.10	2.167E+02
$CH_3SC \cdot H_2 + O_2 \rightarrow CH_3S(=O) + CH_2O$	4.654E+08	0.44	6.12	1.861E+05
$CH_3SC \cdot H_2 + O_2 \rightarrow CH_2S + CH_2O + OH$	2.155E+14	-1.06	6.10	1.540E+07
$CH_3SC \cdot H_2 + O_2 \rightarrow CYCH_2SCH_2O + OH$	3.240E+11	-0.60	11.59	2.838E+01
$CH_3SCH_2OO \cdot \rightarrow CH_3SC \cdot H_2 + O_2$	3.208E+06	1.24	21.22	5.183E-06
$CH_3SCH_2OO \cdot \rightarrow CH_3SC(=O)H + OH$	9.003E-43	13.84	19.32	3.228E-21
$CH_3SCH_2OO \cdot \rightarrow C \cdot H_2SCH_2OOH$	1.252E+08	0.42	16.06	3.513E-03
$CH_3SCH_2OO \cdot \rightarrow CH_3S(=O) + CH_2O$	9.324E-23	8.25	19.27	2.789E-15
$C \cdot H_2SCH_2OOH \rightarrow CH_3SCH_2OO \cdot$	1.538E+11	-0.82	10.03	1.408E+02
$C \cdot H_2SCH_2OOH \rightarrow CH_2S + CH_2O + OH$	7.905E-06	3.65	14.93	7.868E-07
$C \cdot H_2SCH_2OOH \rightarrow CYCH_2SCH_2O + OH$	2.041E-22	7.60	16.17	3.385E-14

**Table B.3** Calculated Reaction Parameters at P=0.1 atm,  $k = A(T)^n \exp(-E_a/RT)$   
(T=200-2000K)

Reaction	$A(\text{s}^{-1})$	$n$	$E_a$ (kcal/mol)	$k_{298} (\text{s}^{-1})$
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{OO}\cdot$	2.741E+67	-18.47	11.61	5.264E+12
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$	2.750E+70	-19.61	14.39	5.984E+10
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$	5.782E+08	0.70	11.14	2.149E+02
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$	8.691E+09	0.07	6.81	1.404E+05
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$	4.029E+17	-1.97	8.51	2.359E+06
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{C}\cdot\text{YCH}_2\text{SCH}_2\text{O} + \text{OH}$	2.904E+13	-1.16	12.67	1.730E+01
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$	4.838E+05	1.95	22.09	7.575E-06
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$	9.078E-38	13.26	20.39	1.812E-18
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$	4.203E+05	1.35	15.81	3.521E-03
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$	3.010E-15	6.73	22.29	6.588E-14
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CH}_3\text{SCH}_2\text{OO}\cdot$	1.067E+23	-4.34	13.81	1.498E+02
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$	1.467E+35	-8.21	27.34	6.540E-06
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{C}\cdot\text{YCH}_2\text{SCH}_2\text{O} + \text{OH}$	2.838E+39	-10.40	34.17	5.371E-12

**Table B.4** Calculated Reaction Parameters at P=10 atm,  $k = A(T)^n \exp(-E_a/RT)$   
(T=200-2000K)

Reaction	$A(\text{s}^{-1})$	$n$	$E_a$ (kcal/mol)	$k_{298} (\text{s}^{-1})$
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{OO}\cdot$	1.120E+60	-15.56	11.13	5.811E+12
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$	1.280E+62	-16.46	15.64	8.212E+08
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$	1.337E+11	0.05	13.08	3.956E+01
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$	2.677E+11	-0.28	9.24	6.267E+03
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$	6.058E+12	-0.29	11.58	1.032E+03
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{C}\cdot\text{YCH}_2\text{SCH}_2\text{O} + \text{OH}$	6.232E+12	-0.76	16.26	3.905E-02
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$	8.786E+36	-7.48	31.72	8.374E-06
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$	2.498E+44	-10.99	44.43	2.549E-16
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$	3.114E+19	-2.89	19.95	3.522E-03
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$	1.810E+39	-9.34	38.83	2.628E-13
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CH}_3\text{SCH}_2\text{OO}\cdot$	4.367E+17	-2.38	13.03	1.510E+02
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$	1.774E+25	-4.24	26.76	9.640E-06
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{C}\cdot\text{YCH}_2\text{SCH}_2\text{O} + \text{OH}$	1.831E+29	-5.90	34.39	1.750E-11

**Table B.5** Calculated Reaction Parameters at P=100 atm,  $k = A(T)^n \exp(-E_a/RT)$  (T=200-2000K)

Reaction	$A(\text{s}^{-1})$	$n$	$E_a$ (kcal/mol)	$k_{298}(\text{s}^{-1})$
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{OO}\cdot$	5.692E+53	-13.34	10.03	5.819E+12
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$	2.570E+52	-13.30	14.41	8.251E+07
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$	6.652E+09	0.50	13.87	4.775E+00
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$	6.769E+08	0.56	9.67	6.624E+02
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$	1.184E+01	3.30	10.35	1.088E+01
$\text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2 \rightarrow \text{CYCH}_2\text{SCH}_2\text{O} + \text{OH}$	4.616E+02	2.39	15.54	4.723E-04
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}\cdot\text{H}_2 + \text{O}_2$	9.819E+31	-5.73	30.87	8.386E-06
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{SC}(=\text{O})\text{H} + \text{OH}$	1.584E+38	-8.56	43.95	3.054E-16
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH}$	4.448E+16	-1.92	19.36	3.522E-03
$\text{CH}_3\text{SCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{S}(=\text{O}) + \text{CH}_2\text{O}$	2.135E+33	-7.15	38.05	2.711E-13
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CH}_3\text{SCH}_2\text{OO}\cdot$	1.302E+15	-1.55	12.44	1.510E+02
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CH}_2\text{S} + \text{CH}_2\text{O} + \text{OH}$	7.724E+18	-2.11	25.34	9.678E-06
$\text{C}\cdot\text{H}_2\text{SCH}_2\text{OOH} \rightarrow \text{CYCH}_2\text{SCH}_2\text{O} + \text{OH}$	5.802E+20	-3.04	32.56	1.773E-11

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