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# Computational and experimental evidence on reaction mechanisms of oxidized sulfur-containing compounds in ground and excited states

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# Computational and experimental evidence on reaction mechanisms of oxidized sulfur-containing compounds in ground and excited states

by

Jerry W. Cubbage

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Organic Chemistry

Major Professor: William S. Jenks

Iowa State University

Ames, Iowa

2001

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Major Professor

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For the Major Program

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For the Graduate College

To
Julia

My best friend!

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# GENERAL INTRODUCTION

## Dissertation Organization

This dissertation is organized into four chapters. Chapter 1 focuses on the thermal elimination of sulfoxides and sulfinyl derivatives and the comparison of computational and experimental studies. Chapter 2 presents the thermolysis of analogous sulfones and classification of this elimination reaction mechanism. To gain insight on the photostereomutation mechanism, a comprehensive computational study of the excited state potentials for $H_2SO$ and DMSO is covered in Chapter 3. The emphasis of Chapter 4 is on the photo-assisted reduction of sulfoxides. Chapters 1, 3, and 4 will be the basis for future publications. Chapter 2 is based on a published paper.

Within Chapter 1, there is a brief review of where this reaction has been used in the synthetic community. There is also a comprehensive introduction to the class of elimination mechanism (Ei reaction) for analogous molecules and sulfoxides. This includes both experimental and computational facts presented in the previous literature on Ei reactions. The results and discussion will present both computational and experimental activation barriers that compare closely for the sulfoxide elimination. While the author completed the great majority of this work, Dr. Yushen Guo initiated the first experimental studies for Chapter 1.

Chapter 2 is an extension of the Ei reaction extensively evaluated in Chapter 1 to sulfone chemistry. A brief introduction discusses the previously known thermal reaction of sulfones. Both computational and experimental results present data that allow classification of this reaction as an Ei reaction. Brian Vos prepared one of the deuterated starting compounds in preparation of the sulfone used in the isotope study.

Switching gears to photochemistry in Chapter 3, the introduction is fairly comprehensive covering both thermal-chemical and photochemical events relevant to stereomutation of sulfoxides. The results present a relatively complicated computational study for $H_2SO$ and DMSO. The discussion focuses on the elucidation of mechanism of photostereomutation. Dr. William Jenks produced some of the optimized geometries used in the study.

In Chapter 4, there is a brief introduction into the chemical reduction of sulfoxides as well as a limited discussion of past photochemical studies. The bulk of this chapter is devoted to results and discussion of various experiments examining the photo-assisted reduction of certain alkyl aryl and diaryl sulfoxides. Troy Tetzlaff and Heather Groundwater in part carried out the work in this chapter.

## Objectives

This dissertation contains an overall theme of deducing reaction mechanisms of sulfur and oxygen containing compounds. The processes in the first two chapters are related by using gas-phase kinetics, isotope effects, and computational chemistry to better understand the mechanism that is operating for the thermolysis of sulfoxides, sulfinyl derivatives, and sulfones. The third chapter is a computation project designed to aid in understanding the details of the mechanism of photostereomutation of sulfoxides. The fourth chapter describes the deduction of the mechanism operating in sulfoxide reduction photochemistry. All in all, this dissertation should provide evidence of the different processes that work either by thermal or photochemical means for sulfur and oxygen containing compounds.

Another underlying theme presented in this dissertation is the relevance and usefulness of computational quantum chemistry to real orgainc systems. It is utilized throughout the first three chapters to aid in the deduction of reaction mechanisms. In the first two chapters, it provided information in the form of transition state geometries, which were previously unknown. It also provided added information on the elimination reaction energetics of molecules that could not be characterized by experiment. In Chapter Three, computational chemistry allowed access to the excited state potential energetics. Excited state geometries, which were previously unknown, are obtained from quantum chemical calculations. The use of computational chemistry also provided information for future experiments. Finally, it is shown in this dissertation the pivotal role computational chemistry can play in deducing reaction mechanisms.

## Nomenclature

Lastly, because of the multitude of sulfur oxidation states, and the relative unfamiliarity of many chemist with their nomenclature, Figure 1 is intended as a quick reference guide. Throughout

this manuscript, sulfoxides have been written in the octet obeying ylide form (see the introduction in Chapter One for an explanation).

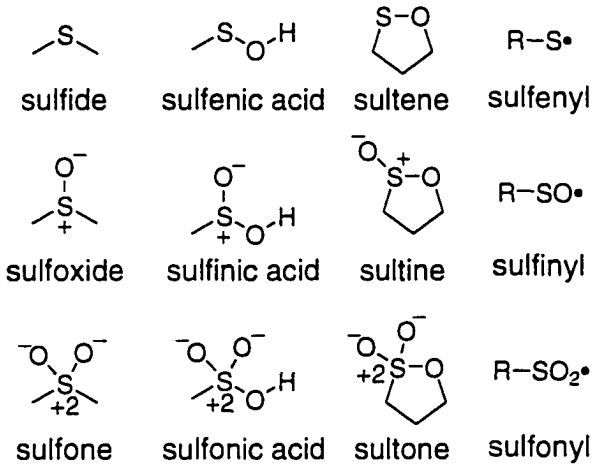


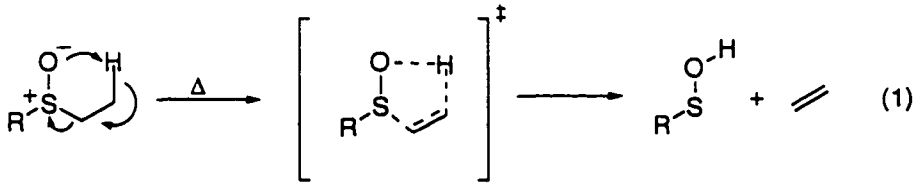

**Figure 1**. Illustrations of sulfur-containing functional groups.

# CHAPTER 1

# THERMOLYSIS OF ALKYL SULFOXIDES AND DERIVATIVES: A COMPARISION OF EXPERIMENT AND THEORY

## Introduction

Thermal or base-catalyzed elimination reactions have been widely used in the preparation of olefins.[1] There are many different elimination mechanisms (E1, E1CB, E2, or Ei) that have been invoked to explain the formation of olefins.[1,2] This chapter focuses on the mechanistic aspects of the pyrolytic gas-phase Ei elimination of alkyl sulfoxides and derivatives. A prototype of the sulfoxide Ei reaction is shown in equation 1.




(1)

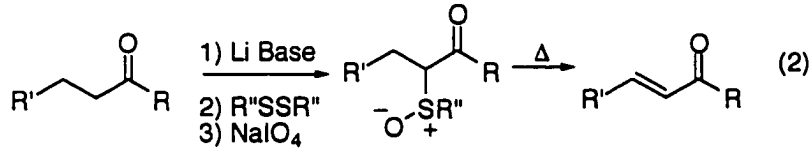
This introduction focuses on the background of internal elimination (Ei) reactions and is divided into two major sections, the first listing previous experimental studies and the second listing previous computational studies. The experimental section begins by presenting the synthetic utility of the sulfoxide elimination. Some divergence from sulfoxide elimination occurs to make reference to various Ei reactions for different type molecules (namely esters, xanthates, and amine oxides). A fairly comprehensive review on the Ei mechanism of amine oxide eliminations is presented since the amine oxides parallel sulfoxides in structure and reactivity. The mechanism section ends with a few other Ei reactions being mentioned. The past studies within each section are presented roughly in chronological order, though observations that are obviously tied to one another are discussed together.

The computational section presents a brief discussion on the calculation of hypervalent molecules since one representation of a sulfoxide is in hypervalent form. This is followed by calculations on amine oxides since computational background on the sulfoxide elimination is limited. Parallels are drawn to the amine oxide computational studies from the calculations of sulfoxides presented in this chapter.

## Historic Background

### Experimental Studies

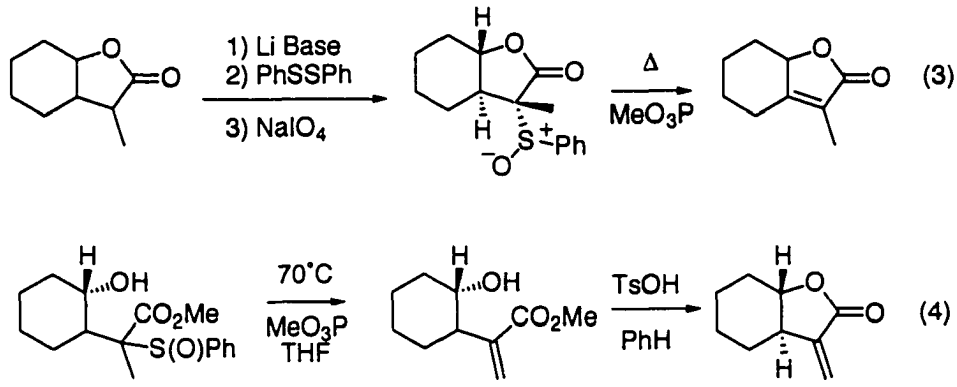
**Synthetic Considerations.**[3] In an early use of the sulfoxide Ei reaction in synthesis, Jones et al. pyrolized 3-alkylsulfinyl-5α-cholestanes to provide regiospecific olefins in the steroidal system.[4,5] Trost and Salzmann developed this as a method for induction of unsaturation and brought it to a synthetically useful level (equation 2).[6] This was first carried out to prepare α,β-unsaturated esters and then quickly extended to ketones.[7] It was realized that the carbonyl facilitates the Ei reaction allowing the elimination to take place at much lower temperatures. The use of benzenesulfinyl substrate over methanesulfinyl substrate also reduced the temperature necessary for the Ei reaction.[8,9] To make the reaction more synthetically useful, trimethylphosphite was employed as a sulfenic acid trap.




(2)

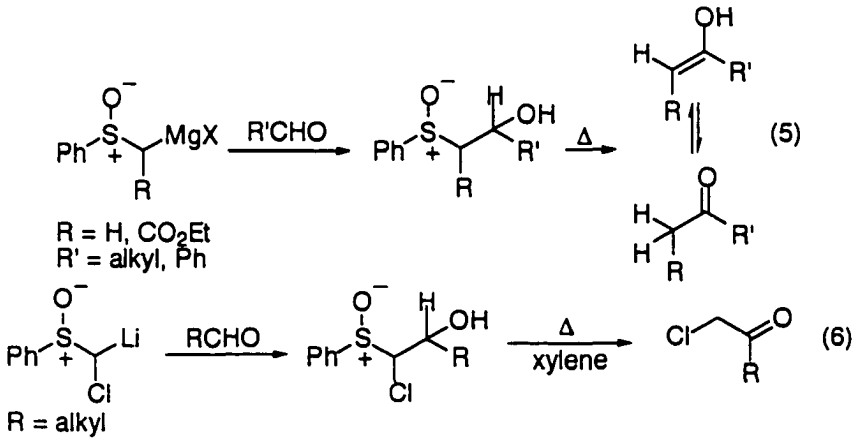
R = alkoxy, alkyl, aryl
R' = alkyl, aryl
R" = Ph, Me

The synthesis of endocyclic and exocyclic olefins in bicyclic lactone systems were carried out using the regioselectivity of the syn-elimination for placement of the double bond.[8] In equation 3, the synthesis of the endocyclic olefin was straightforward. However, the synthesis of the methylene-γ-butyrolactone was not as convenient (equation 4). The exocyclic olefin was formed and then the lactonization was carried out to form the α-methylene bicyclic lactone. Trost's group has demonstrated the mildness of the syn-elimination. His group has provided several examples with




many functional groups contained within the molecules.[10] Molecules from steroids and bug hormones have been completed with the elimination as the key step.[9]

Nokami et al. pyrolyzed β-hydroxy sulfoxides to gain access to β-keto esters and methyl ketones.[11] The β-hydroxy sulfoxides were prepared via the reaction of a Grignard reagent with the appropriate aldehydes. The elimination produced β-keto esters and methyl ketones in good yield (74-95%). The reaction affording the β-keto esters and methyl ketones is shown in equation 5. Reutrakul and Kanghae have used a similar approach in the synthesis of α-chloromethylketones (equation 6).[12] The α-chloro-β-hydroxy sulfoxides and α-chloromethylketones were both isolated in good yield (66-72% and 76-95%, respectively).



Allyl alcohols have been converted to 1,3-dienes by sulfenate-sulfoxide [2,3] sigmatropic rearragement follow by syn-elimination (Figure 1).[13] Several 1,3-dienes were prepared in moderate to good yields (50 – 100%) with this one-pot sequence. 2,4-Dinitrobenzene-sulfenyl chloride was employed since it was found to be the easiest sulfenyl chloride to handled and allowed lower temperature for the thermal syn-elimination.

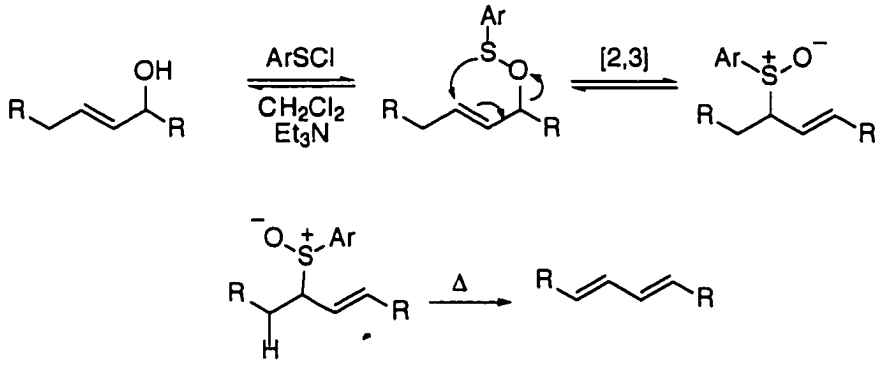
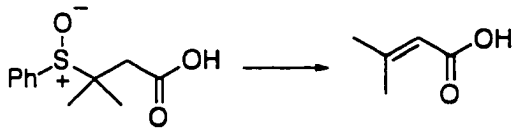



**Figure 1**. Sequential [2,3] sigmatropic rearragement followed by syn-elimination

Microwave irradiation has been employed to make olefins, ketones, and an unsaturated acid in almost quantitative yields at much reduced reaction times.[14] An example comparing the microwave product yield versus the thermal product yield is shown in equation 7. This yield is typical for the series of compound prepared. The thermal reaction was run for 24 hours, whereas, the microwave reaction was run for one minute. All reactions were carried out in N-methylformamide.

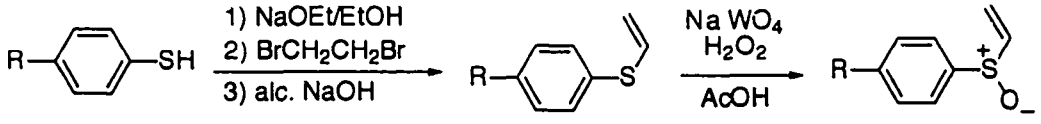



| Yields | |
|---|---|
| Thermal | Microwave |
| 45% | 99% |

(7)

The thermal degradation of substituted poly(aryl vinyl sulfoxides) has been shown to produced all-trans-polyacetylene.[15] Three aryl vinyl sulfoxides were prepared as presented in Figure 2 and polymerized with anioinic initiator (3-methyl-1,1-diphenylpentyl)lithium. Degradation to form all-trans-polyacetylene was carried out between 70 – 120 °C and relative rates were measured at 10 °C increments (equation 8). It was found that substituents reacted in the order of Cl > F> OMe. The

authors observed an induction period over the first 50 min and rationalized this as a "zipper-type" mechanism. Once one double bond is formed each double bond can be formed faster due to the conjugative effects until the limiting rate is achieved. The all-trans-polyacetylene formation was rationalized from the minimization for steric interaction of the polymer chains and produced polymers with weights ($M_w$) on the order of 10000. (Figure 3).



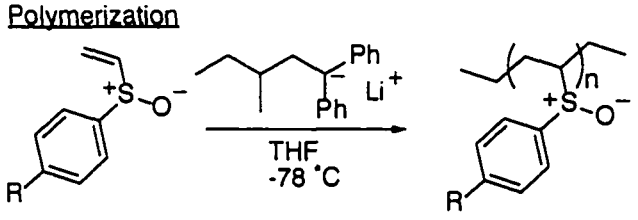
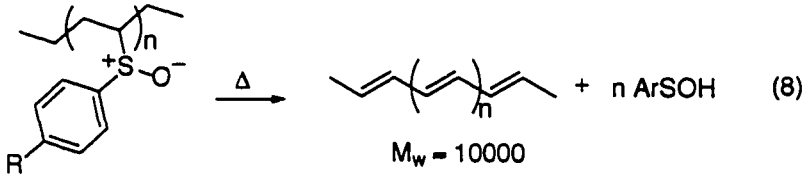




**Figure 2.** Sythesis and polymerization of aryl vinyl sulfoxides



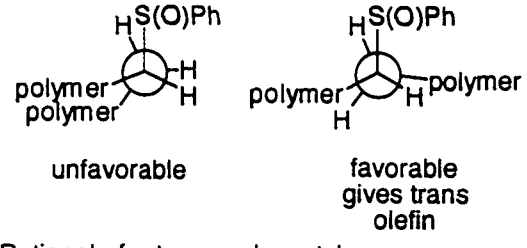




**Figure 3.** Rationale for trans-polyacetylene

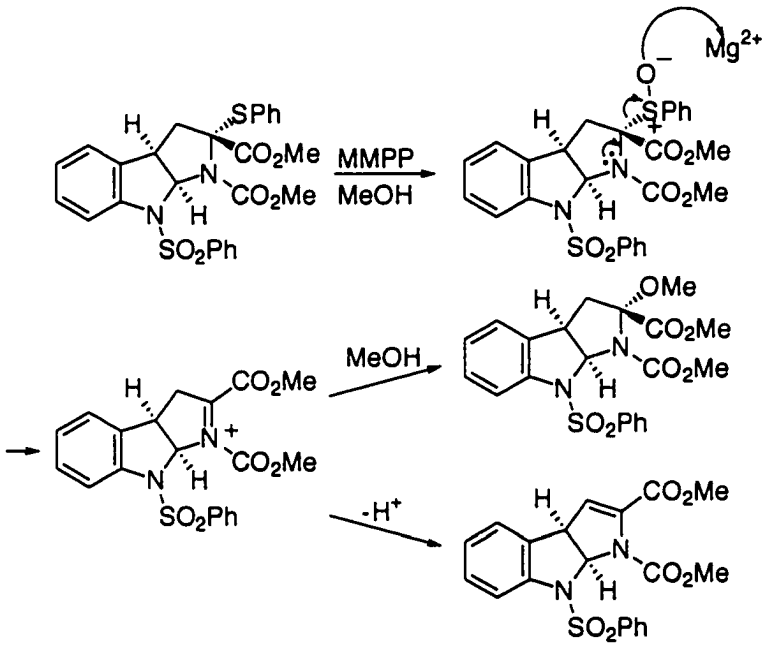
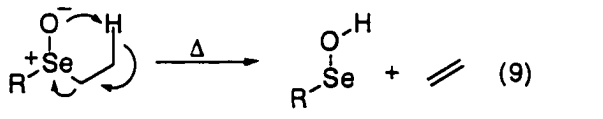



**Figure 4**. Proposed stepwise mechanism with MMPP

As one of the steps in the synthesis of cyclic tautormers of tryptophan, Bruncko and Crich employed the syn-elimination reaction.[16] They discovered that with the oxidation of the sulfide to the sulfoxide with magnesium monoperoxyphthalate hexahydrate (MMPP) in MeOH, the elimination reaction occurred at room temperature overnight and in 72% yield of the dehydro derivative. The authors proposed that the elimination occurred via a stepwise mechanism, since products derived from trapping by solvent were isolated as shown above in Figure 4. The elimination of the bezenesulfinyl group was aided by a Lewis acid interaction with magnesium. When sulfur is replaced by selenium, the reaction only produces the dehydro derivative in quantitative yield.

Selenium oxide chemistry has been a valuable companion to the sulfoxide chemistry for synthetic preparation of olefins (equation 9).[17] The syn-elimination of selenoxides occurs at much lower temperatures than the sulfoxide elimination. This method has generally replaced the sulfoxide elimination for the formation of unsaturated ketones and esters even though the selenium chemistry is know to be much more toxic and unpleasant to work with.[18,19] Sharpless and Lauer have used the selenium chemistry to prepare allylic alcohols.[20]



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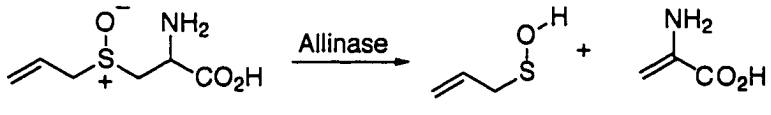

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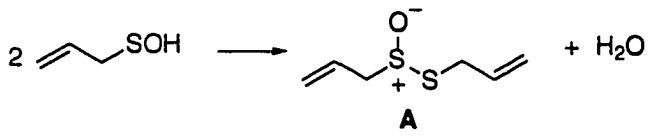


**A**

**Sulfinyl Derivatives.** In a study on the antithrombotic agent from garlic, Block et al. have implicated the Ei reaction of sulfoxides and thiosulfinates to play an important role in formation of the anti-blood clotting molecule (E, Z)-Ajoene.[21,22] Garlic was found to contain S-allylcysteine S-oxide (alliin), which is converted by the enzyme allinase to allyl 2-propenethiosulfinate (**A**) (equation 10). Figure 5 shows the cascade of reactions proceeding from allyl 2-propenethiosulfinate (**A**). Thiosulfinate **A** condenses with subsequent loss of 2-propenesulfenic acid to cation **B**. Cation **B** then eliminates 2-propenesulfenic acid to produce cation **C**. Finally, addition of 2-propenesulfenic acid across the double of cation **C** forms molecule (E, Z)-Ajoene (**D**).

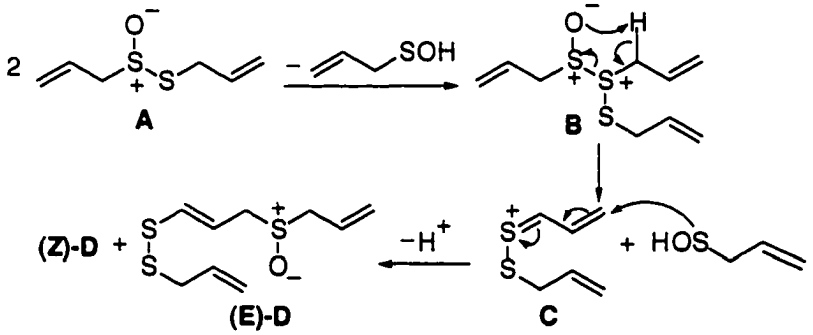
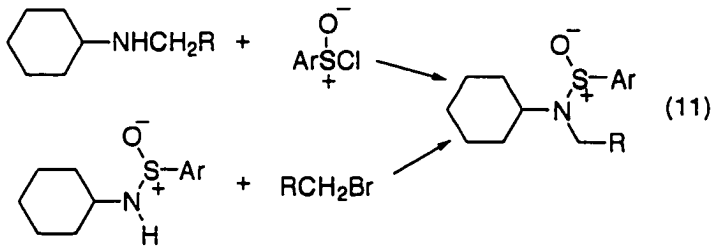
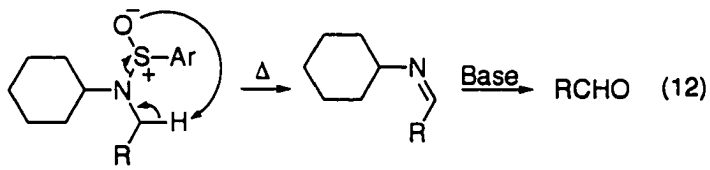


**Figure 5**. Reaction sequence for the formation of (E,Z)-Ajoene (**D**)

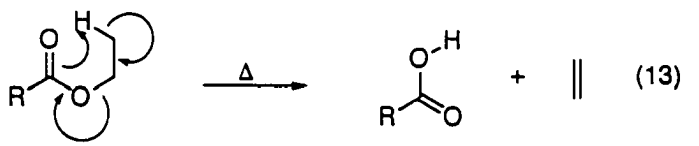
The Ei reaction of sulfinamides was utilized by Trost and Liu to produce imines, which were subsequently hydrolzed to the corresponding aldehydes.[23] Sulfinamides were prepared by two methods: coupling of an secondary amine with the corresponding arenesulfinyl chloride or alkylation of bezenesulfinamide with benzyl or allyl bromides (equation 11). The authors suggested that the

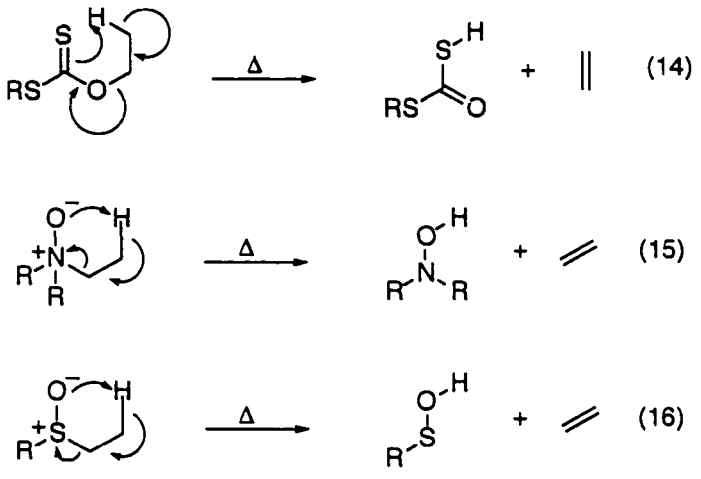
elimination required much higher temperatures than did the thiosulfinates because the N-S bond is quite strong in sulfinamides (refluxing o-xylene). The reaction initially gave the alkyl cyclohexylimine that was isolated by distillation in one instance, but in all other instances, hydrolyzed during workup to the aldehyde in moderate to good yields (equation 12).




**General Ei Mechanistic Background**. In order for an Ei reaction to be claimed as a reactive mechanism, the substrate must contain a cis-β-hydrogen to be transferred in a cyclic transition state (TS) to the substituent acting as the leaving group. The reaction must also display first order kinetics and be not slowed by free-radical inhibitors. A few classes of compounds which have been shown to undergo Ei eliminations during pyrolysis are esters (400 - 600 °C), xanthates (150 - 250 °C)(Chugaev reaction), amine oxides (85 - 150 °C) (Cope elimination), and sulfoxides (80 - 250 °C) (equations 13, 14, 15, and 16, respectively).[24] Both the ester and xanthate eliminations proceed through a six-membered transition state, where as the amine oxides and sulfoxides eliminate through a five-membered transition state.






In further classifying elimination semantics of Ei eliminations, one can considered some syn-eliminations to be "psuedopericyclic"[25] but not pericyclic in nature, although there is a cyclic array of curvy arrows, there is an orbital disconnection between oxygen's electrons and the orbitals are used to transfer the hydrogen. An example of the orbitals used in a pericyclic reaction and a psuedopericyclic reaction is shown in Figure 6. Eliminations can be considered pericyclic only if there is cyclic loop of interacting pi electrons moving in concert.[26]

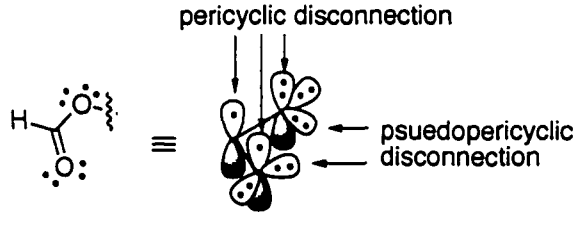



**Figure 6.** The orbitals and electrons of esters. If a reaction involves the pi system it is pericyclic, but if the breaking bond and the lone pair do not overlap the reaction is psuedopericyclic.[27]

The term psuedopericyclic reaction was coined by Lemal in 1976 and classifying reactions of this type has been developed by Birney and others recently.[25,27-30] The original example of a psuedopericyclic reaction as discovered in the Lemal laboratory is shown in Figure 7. The sulfoxide "automerization" of perfluorotetramethyl thiophene exo-S-oxides is not a four electron [1,3] sigmatropic rearrangement or a biradical process. Due to a very low barrier ($\Delta G^{\ddagger}$ = 6.8 kcal/mol), a six electron process has been supposed to operate with the endocyclic lone pair participating

nucleophilically in the walk around the ring. A key point regarding psuedopericyclic reactions is that the "orbital disconnect" frees the reactions from orbital symmetry constraints. They are thus not "forbidden" depending on the number of electrons.

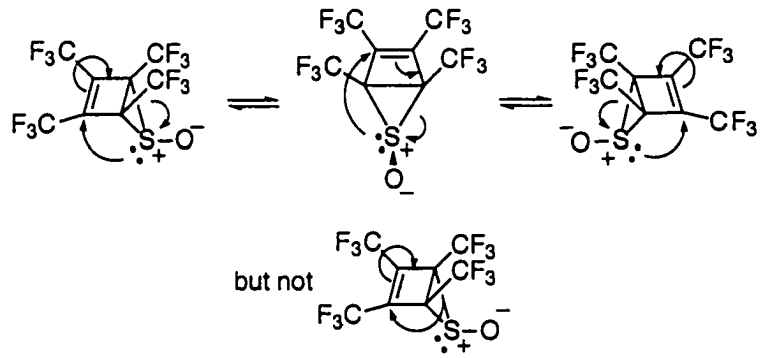
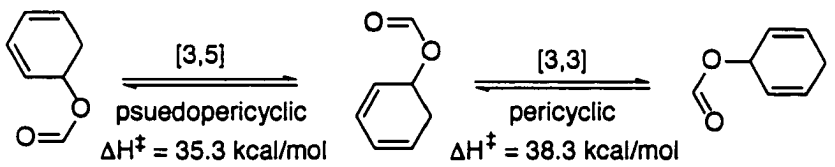


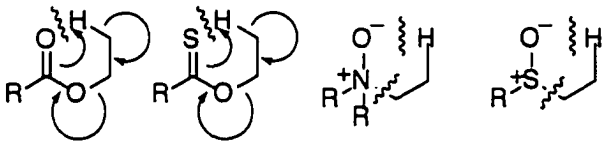

**Figure 7**. The original psuedopericyclic reaction[25]

Birney and co-workers have stated that most psuedopericyclic reactions occur through planar transition states with barriers lower than the corresponding pericyclic reaction for the same substrate.[27] An example of a reaction that can choose between a psuedopericyclic or a pericyclic pathway is shown in equation 17. The authors have found that the [3,5] psuedopericyclic pathway has a barrier 3 kcal/mol lower in energy than the [3,3] pericyclic pathway.




(17)

**Elimination of esters and xanthates**. From the above description of psuedopericyclic mechanism, it is interesting classify the elimination of esters and xanthates into that mechanistic category, although there has been no previous support for that in the literature beyond the obvious connection to Birney's ester pyrolyses. This is suggested since there is a cyclic loop of electron flow with only one orbital disconnection (Figure 8).



ester xanthate amine oxide sulfoxide

**Figure 8.** The squiggly lines represent orbital disconnections that arise during Ei reactions.

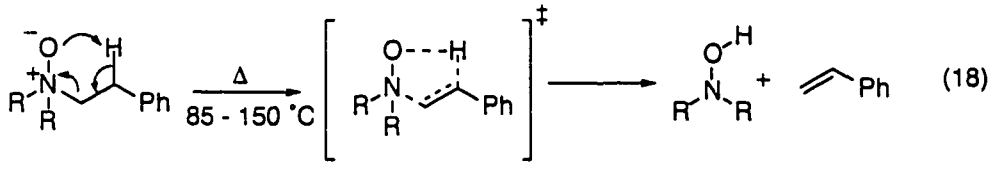
The pyrolysis of esters (equation 13) has been studied in the gas phase and the activation energy ($E_a$) has been determined from Arrhenius plots.[31] Various substituted alkyl esters have been investigated and they all have produced olefins with activation energies in the range of 40 to 50 kcal/mol. Ordinary alkyl esters react slower (higher $E_a$) than bulky t-butyl esters (e.g. ethyl acetate eliminates 1200 times slower than t-butyl acetate at 500 °C). This rate difference is due to the bigger group being better at stabilizing the slight carbonium-ion build-up in the transition state. A deuterium isotope ($k_H/k_D$ = 2.1) has been determined for the ethyl acetate elimination at 500 °C.

In the xanthate elimination (equation 14), the initial acid that is produced is unstable and forms a thiol and carbon oxysulfide. Arrhenius parameters have been determined for the elimination with cholesteryl esters and corresponding cholesteryl xanthates. The xanthates eliminated with a barrier 11 kcal/mol lower than the esters.[31] This difference in activation barrier is in part due to the strength of the acid formed (better leaving group). The initial acid formed in the xanthate elimination is suggested to be stronger than acetic acid that is formed with the ester pyrolysis. An additional factor involved favoring the xanthate elimination over the ester pyrolysis is that the S=C bond is sacrificed while gaining O=C bond in the acid. This process is exothermic by roughly 20 kcal/mol. This is probably more than enough energy to account for the 11 kcal/mol barrier difference between the xanthates and the esters.

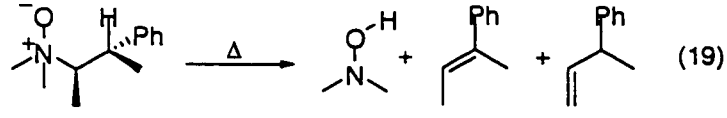
The other two families of elimination reactions, amine oxides and sulfoxides, are structurally comparable, as were the esters and xanthates. The amine oxides and sulfoxides resemble each other in functionality. The N-O bond in amine oxides is an obligate ylide. As discussed later in the introduction of this chapter we believe the sulfoxide's S-O bond is also best described that way. Unlike the esters and xanthates, all of the amine oxide and sulfoxide eliminations occur through a 5-membered cyclic syn-periplanar transition state and should not be considered psuedopericyclic or

pericyclic in nature. The elimination reaction of amine oxides and sulfoxides will contain two orbital disconnections as shown above in Figure 8. These reactions should however be considered be intramolecular eliminations with internal bases.

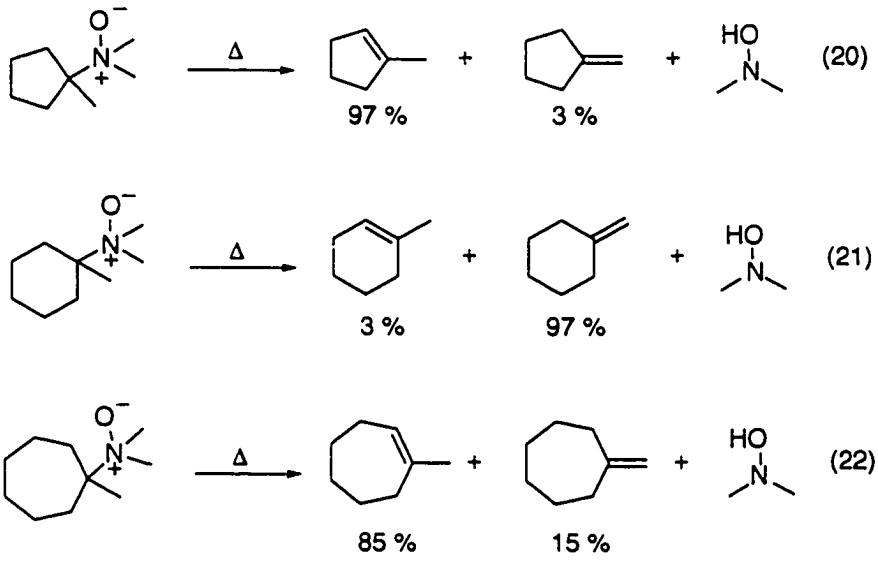
**Amine Oxides.**[32] The first amine oxide elimination was reported by Cope and co-workers in 1949.[33] Unsymmetrical amine oxides were investigated and the product distributions were roughly determined by the number of available β-hydrogens on either substituents.[34] The order of ease of elimination (faster rate), corrected for the number of β-hydrogens, to form olefins is 2-phenylethyl > t-butyl >> ethyl > isopropyl ~ n-decyl > n-butyl > isoamyl > ethyl > n-propyl groups. The 2-phenylethyl example is shown in equation 18. Both t-butyl and 2-phenylethyl varied significantly in the rate of elimination from the other alkyl groups through the relief of steric strain and the acidity of β-hydrogen atom, respectively.[35] An additional explanation for the faster rate of reaction with the 2-phenylethyl substrate is that the transition state is being stabilized by developing conjugation with the phenyl group in forming the olefin. Activation energies for 2-phenylethyl and 2-phenylpropyldimethylamine oxides are 24 – 30 kcal/mol and have small primary isotope effects ($k_H/k_D$ = 2.3 – 3.4, observed at 60 °C) depending on the solvent mixture.



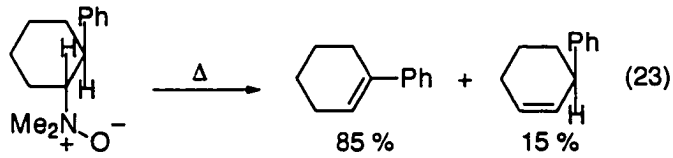

Cram and co-workers have shown the alkyl amine oxide elimination to be stereospecific from their study with threo- and erythro-N,N-dimethyl-3-phenyl-2-butylamine oxide. The threo case produced cis-2-phenyl-2-butene and the erythro case produced the trans olefin.[36] The threo elimination is shown in equation 19. Both systems produced the less substituted olefin, 3-phenyl-1-butene, in small amounts.



The Cope group studied the elimination of alicyclic amine oxides.[37] N,N-dimethyl-1-methylcycloalkylamines oxides containing five-, six-, and seven-membered rings were evaluated (equations 20, 21, and 22, respectively). The variation in endocyclic/exocyclic product ratio with ring size was interpreted on a case by case basis. The low energy conformation of the five-membered ring compound is thought to force the oxygen atom into essentially the perfect position for endocyclic olefin formation. In the six-membered ring case, it is proposed that a boat confromation is required for endocyclic elimination. The seven-membered case produced the endocyclic product since the ring was more flexible than the smaller rings, thus reducing the ring strain in aligning the N-O with the hydrogen. The medium sized rings of eight-, nine-, and ten-membered were also investigated and found to give predominately the endocyclic olefins will only small amounts of the methylenecycloalkane being formed.[38]




The stereochemistry of the elimination of amine oxides has been demonstrated to be syn (or cis) through pyrolysis of cis- and trans-2-phenylcyclohexyldimetylamine oxides (equations 23 and 24) and isotope studies. In equation 23, the amine oxide has a choice of two syn-hydrogens and the reaction proceeds in producing more of the conjugated olefin, whereas in equation 24, the amine oxide only has one syn-hydrogen and exclusively that olefin is formed[39]

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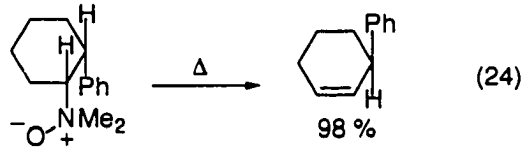
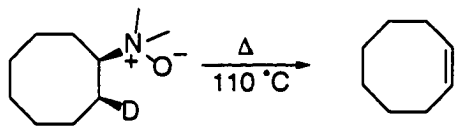


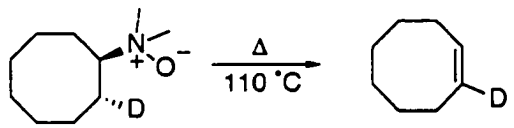

(24)

Bach and co-workers have investigated primary and secondary isotope effects in the amine oxide elimination affording apopinene[40] and a primary isotope effect in cis- and trans-N,N-dimethylcyclooctyl oxide-2-$d_1$.[41] In the latter case, the primary isotope effect was determined to be 3.5 at 110 °C on the bases of deuterium content from mass spectral analysis (equations 25 and 26). In the elimination to form apopinene, they found a primary isotope effect of 2.2 and a secondary isotope effect of 1.061 at 120 °C (equation 27). These data are consistent with the syn-hydrogen being transferred in the transition state.



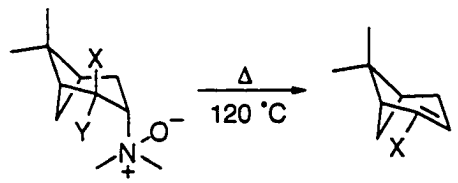

(78% $d_1$, 22% $d_0$)

(25)




(99% $d_1$)

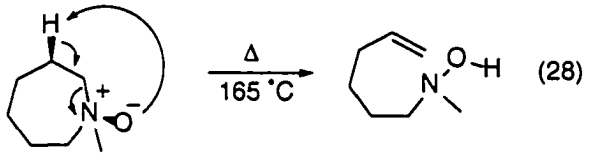
(26)



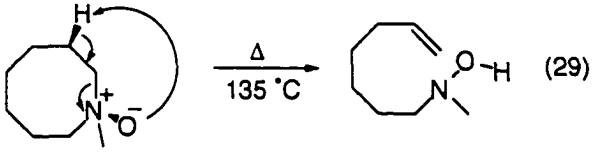

X = H, Y = D $1^\circ$ $k_H/k_D$ = 2.23
X = D, Y = H $2^\circ$ $k_H/k_D$ = 1.061

(27)

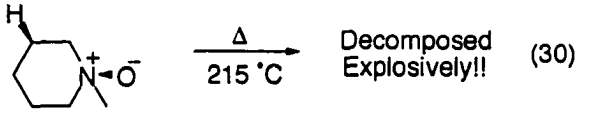
Ring cleavage of amine oxides was investigated.[42] The ring cleavage reaction was found not to occur with six-membered rings, but when increasing the ring size to seven- and eight-membered, the reaction became facile (equations 28 and 29, respectively). The six-membered ring upon heating to over 200 °C was found to violently decompose to gaseous products. This was rationalized by noting that the ring was not flexible enough to adopt the syn-periplanar conformation to transfer the hydrogen (equation 30). Equation 31 shows the α-methyl derivative, a cousin to the six-membered ring, was able to undergo the elimination to produced the unsaturated hydroxylamine, since the external methyl and the amine oxide could adopt the correct elimination conformation.



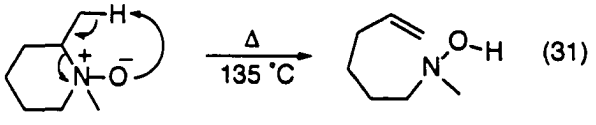

(28)




(29)

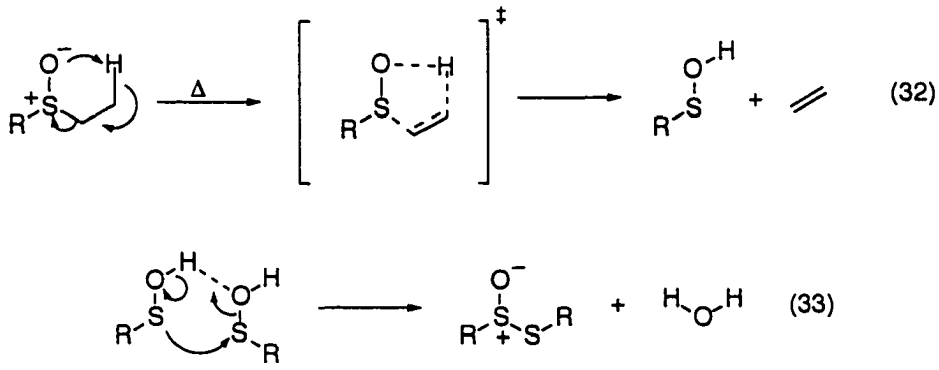



(30)




(31)

**Sulfoxides.**[43] Sulfoxides undergo many of the same reactions as amine oxides and the mechanism has been rationalized with many of the same tests. The pyrolyses of sulfoxides produces sulfenic acids and olefins (equation 32). Unlike the amine oxide case that affords a stable hydroxylamine, sulfenic acids are unstable, and are usually isolated as their anhydrides (thiosulfinates) (equation 33).[44] Both gas phase and solution reactions display first order kinetics and are thought to go through a cyclic planar transition state.



(32)



(33)

**Mechanistic Considerations**. In 1960, Kingsbury and Cram investigated the thermolysis of four diastereomeric 1,2-diphenyl-1-propyl phenyl sulfoxides at 80 °C and at 120 °C.[45] Each diastereomer was separated and pyrolized. The authors found little effect of solvent on the elimination. Two of the diastereomers were evaluated at three temperatures in the range of 70 – 110 °C. Curved Eyring plots were observed in going from low to high temperatures. Therefore, two activation enthalpies were determined to range from 26 to 30 kcal/mol and activation entropies ranged from -6 - +5 e.u. These results, combined with the loss of stereospecificity in olefin formation at 120 °C, led the authors to propose two operating mechanisms (Figure 9). At the lower temperature, their results were found to be stereospecific and consistent with a five center concerted cyclic transition state. However, they proposed that a radical pair was formed at the higher temperature that disproportionated by hydrogen atom transfer to give both possible olefins. These results varied from the results with similar threo- and erythro-amine oxides in which the elimination was totally stereospecific.[36]

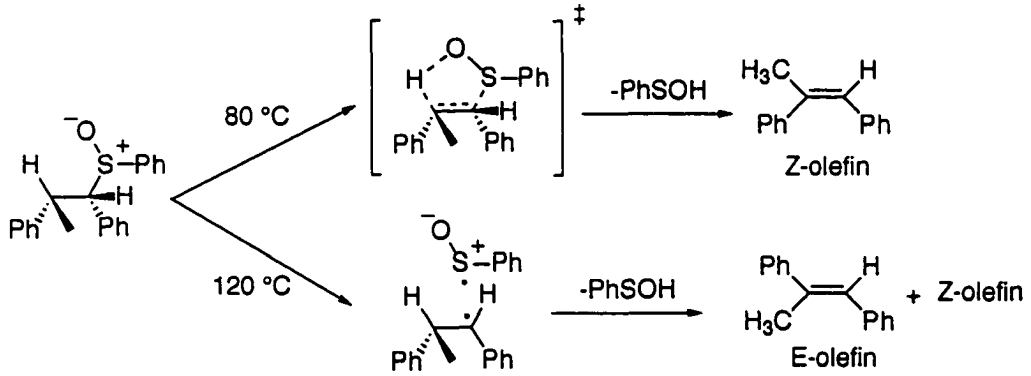



**Figure 9**. Mechanisms of the thermolysis of diasteromeric sulfoxides

Since 1960 there hasn't been convincing evidence for the radical mechanism, which may depend on the presence of all three phenyl groups or at least the sulfoxide in Figure 9. Evidence to support the syn-elimination mechanism was found with the pyrolysis of unsymmetrical dialkyl sulfoxides.[46] Emerson and co-workers analyzed the gaseous alkenes produced from the thermolysis of various alkyl sulfoxides. They found the overall rate for the formation of alkene was enhanced with the more substituted carbon substituent (e.g. sec-butyl ethyl sulfoxide eliminated faster than n-butyl ethyl sulfoxide). Activation enthalpies were determined and were all in range of 30 kcal/mol. The activation entropies were between –3.6 and –17 cal/K*mol, indicative of an ordered cyclic five-membered transition state. Entwistle and co-workers evaluated the products from aryl-substitued alkyl methyl sulfoxides under pyrolytic conditions (160° - 180°C, without solvent).[47] The sulfoxides that contained a β-hydrogen underwent syn-elimination cleanly. In a side-bar to Walling and Bollyky's study on the addition of dimethyl sulfoxide anion to olefins, they investigated the pyrolysis of methyl 3-phenylpropyl sulfoxide in diglyme, which produces allyl benzene with an activation energy of 31.6 ± 3 kcal/mol.[48]

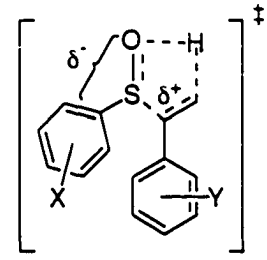



**Figure 10**. Charge distribution in the aryl n-propyl sulfoxide's transition state as proposed by Emerson et al. [49] and Yoshimura et al.[50]

The formation of propene from aryl propyl sulfoxides in phenyl ether solution was evaluated. Emerson and Korniski correlated substituent effects with the rate of reaction.[49] The Hammett plots with substituents in the X-position in Figure 10 revealed a positive ρ–value. The authors found that electron-withdrawing substituents facilitated the reaction rate where as electron-donating substituents slowed the reaction rate. The activation enthalpies and entropies ranged from 25 to 28 kcal/mol and from –11.5 to –16 cal/K*mol, respectively. They suggested that the elimination reaction

occurred through a highly ordered, cyclic transition state with a slight negative charge build-up on sulfur and slight positive charge on carbon (Figure 10).

In study related to Emerson and Korniski's investigation, Yoshimura and co-workers studied the decomposition of substituted 1-phenylethyl phenyl sulfoxides in dioxane solution.[50] Hammett plots with substituents in both in X and Y postions in Figure 10 showed small substituents effects in agreement with Emerson and Korniski. In addition, they carried out an isotope study and found a large kinetic istope effect ($k_H/k_D$ = 4 – 6 observed in the range of 80 – 100 °C). The authors suggested that the thermolysis of the substituted sulfoxides occurred via a concerted mechanism where the transition state varied from one with much charge build-up (E1-like) to one that was nearly synchronous depending on the substituents. Electron-withdrawing groups in position Y in Figure 10 were shown to facilitate the latter type transition state. The relative rates of elimination corrected for the number of β-hydrogens at 100 °C were also evaluated for ethyl phenyl sulfoxide, erythro- and threo-1-phenylethyl phenyl sulfoxides, and 2-phenylethyl phenyl sulfoxides (Figure 11). They found that the threo-1-phenyl substituent produced styrene 264 times faster than having no phenyl groups. Therefore, the phenyl group is stabilizing the C-S bond cleavage in the transition state.

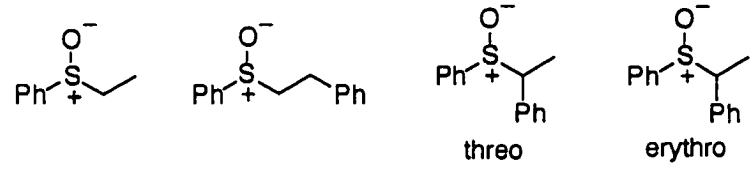


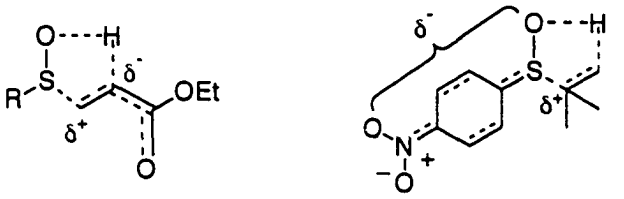

**Figure 11**. Effect of phenyl group placement on the rate of elimination at 100 °C

Shelton and Davis studied the factors that influence the rate of decomposition of dialkyl and alkyl aryl sulfoxides.[51] They have also characterized the formation of the sulfenic acid arising from the decomposition of di-t-butyl sulfoxide.[52] Di-t-butyl sulfoxide was shown to eliminate 93 times faster than methyl t-butyl sulfoxide at 100 °C. This effect was attributed to a large steric interaction stabilizing the transition state. Activation parameters were determined for the thermolysis of di-t-butyl sulfoxide in toluene. At lower temperatures (68 – 90 °C), $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were 25.4 ± 0.7 kcal/mol and –5.0 ± 1.7 e.u., respectively, and at higher temperatures (90 – 100 °C) an increase in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ was observed

(30.2 ± 1.6 kcal/mol and +8.2 ± 4.3 eu, respectively). This indicates a change in mechanism at the higher temperature. The authors postulated from the positive entropy value a much looser less concerted reaction (more E1-like) at the higher temperatures. Although the radical mechanism was not considered, it would be possible to observe the same positive entropy effect if the radical mechanism is operative.

In another study utilizing di-t-butyl sulfoxide pyrolyzed in n-decane, Janssen and Kwart, observed a large isotope effect ($k_H/k_D$ = 5 in the temperature range of 100 – 145 °C) and activation energies of 29.4 ± 0.9 and 32.6 ± 0.9 kcal/mol were obtained for the all proton and the $d_9$ analogue, respectively.[53] Kwart argued that the corset effect[54] is operating to narrow the barrier for the proton transfer to occur via tunneling and that tunneling is the change in mechanism at higher temperatures that was observed by Shelton and Davis.[51]

Shelton and Davis also studied the rate of elimination in formation of α,β-unstaturated esters.[51] A rate acceleration of a factor of about 300 was observed for n-heptyl 2-carboethoxyethyl sulfoxide and ethyl 2-carboethoxyethyl sulfoxide over methyl t-butyl sulfoxide. The authors' explanation for this effect lies in the carbonyl stabilizing the developing the carbanion in the transition state (Figure 12).



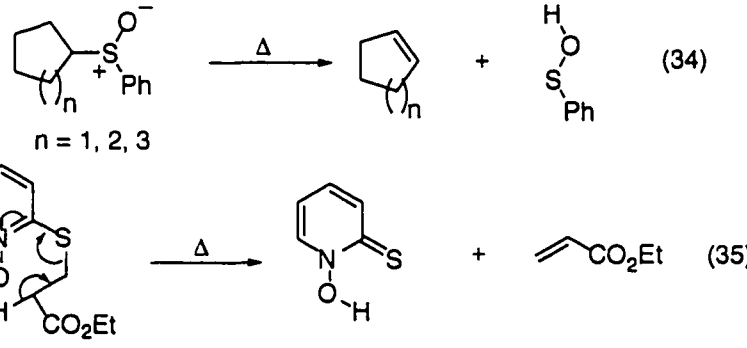

Carbanion stabilization

Resonance stabilization

**Figure 12.** Transition states attributing to rate acceleration

In the same paper, Shelton and Davis compared the substituent effects on the elimination para and meta substituted aryl t-butyl sulfoxides in toluene utilizing a Hammett study. They found a positive ρ-value (+0.695) showing that electron-withdrawing substituents facilitate the reaction as seen in studies presented above by Emerson et al.[49] and Yoshimura et al.[50] The rate constant for t-butyl p-nitrophenyl sulfoxide was far removed from the least-square fit. Extended conjugation was given as an explanation of this result (Figure 12).

Kice and Campbell studied the effect of ring size on the rate of pyrolysis of cycloalkyl phenyl sulfoxides.[55] The sulfoxides investigated contained five-, six-, and seven-membered rings and produced the corresponding cycloalkenes (equation 34). The relative rates were measured at 130 °C. The study resulted in cycloheptyl phenyl sulfoxide reacting 120 times faster than cyclohexyl phenyl sulfoxide. Intermediate in reaction rate was cyclopentyl phenyl sulfoxide, reacting 25 times faster than cyclohexyl phenyl sulfoxide. The elimination rates reflect, as in the elimination of alicyclic amine oxides, that the flexibility of the ring is important in order to form the correct conformation in the transition state for elimination.




when R = alkyl or phenyl Ei reaction doesn't result!

In the Ei reaction of sulfoxides, the oxygen atom of the sulfinyl group must be acting as the internal base. Therefore, the acidity of the β-hydrogen should have an effect on the reaction rate. Crich and Lim have studied this effect.[56] They were in the quest to develop a new elimination reaction with 2-alkythiopyridine N-oxides (equation 35, above). Only the N-oxide substrate containing an acidic β-hydrogen underwent Ei elimination. To further test this result, four sulfoxides were prepared and co-pyrolized without solvent at 70 °C (Figure 13). They found the reaction of the sulfoxide **A** to react at a faster rate of formation of olefin than sulfoxide **B**. Even though the β-hydrogen in sulfoxide **B** be would be expected to be slightly more acidic, the faster rate was observed in sulfoxide **A**. Sulfoxide **A** can stabilize the partial positive charge in the transition state (secondary benzylic cation-like TS) better than sulfoxide **B**. This result is consistent with the study of aryl alkyl sulfoxides

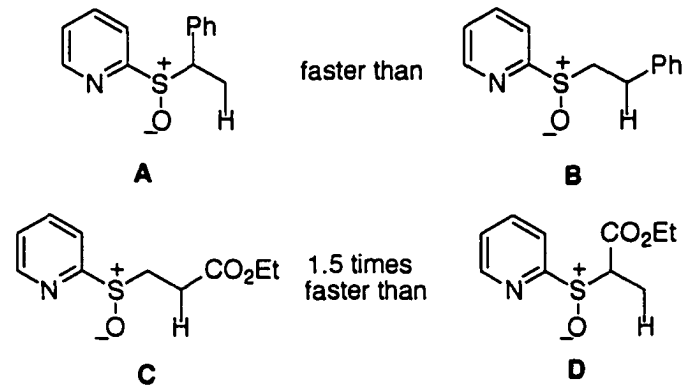
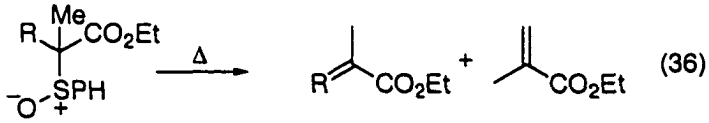



**Figure 13.** Effect of acidity on the Ei reaction

conducted by Yoshmira and colleagues.[50] Comparing sulfoxides **C** and **D**, sulfoxide **C** was found to eliminate 1.5 times faster than sulfoxide **D**. Crich rationalize this faster rate, albeit small, was due to the increase acidity of the β-hydrogen.

Trost and co-workers evaluated the regiospecificity of the Ei reaction in the preparation of unsaturated esters and found that dipole-dipole interactions are important in addition to steric interactions, β-proton acidity, and double bond stability.[7,8] Allyl and propargyl groups beta to the sulfinyl group facilitate the elimination to produce conjugated olefins (equation 36). They also discovered a high preference for endocyclic olefin formation with 2-alkylsulfinyl 2-alkylcycloalkanones and 2-alkylsulfinyl 2-alkyllactones (Figure 14). They suggested the conformation of the sulfinyl group relative to the β-proton in the starting material determines which olefin is formed. The decomposition of unseparated diastereomers of 3-methanesulfinyl-3-methyl-4,5-dihydro-2-furanone in Figure 14 yield the endocyclic olefin in 87% (due to the favorable dipole-dipole interaction) and the exocyclic olefin in 13%.[8] In acyclic versions (esters), formation of the α-methylene group was always produced in excess over the internal olefin (equation 36).




R = allyl ~ propargyl > benzyl ~ methyl >
1° alkyl (methylene) >> 2° alkyl (methine)

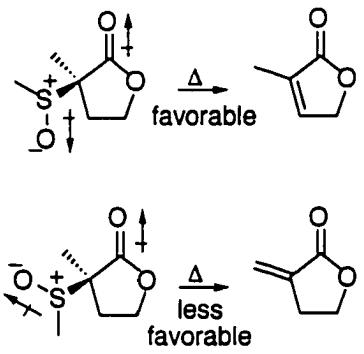
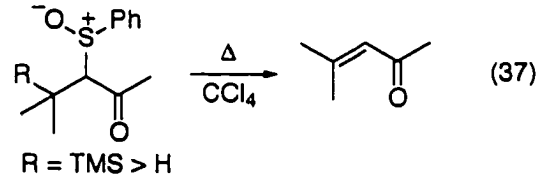



**Figure 14.** Dipole-dipole explanation for the formation of endocyclic vs. exocyclic olefins

The syn-elimination of a β-silyl group was compared to the traditional β-hydrogen elimination in sulfoxides in the preparation of enones.[57] The loss of the β-silyl group was approximately three times faster than that of the analogous β-hydrogen reaction at 90°C in carbon tetrachloride (equation 37). Alkynes were afforded by the loss of the syn-β-silyl group but not the trans-β-silyl group when pyrolyzed neat (Figure 15). If the β-silylsulfoxide also contained a β-hydrogen (α to the silyl group) only the β-hydrogen was quickly lost providing β-silylenones (equation 38).




(37)

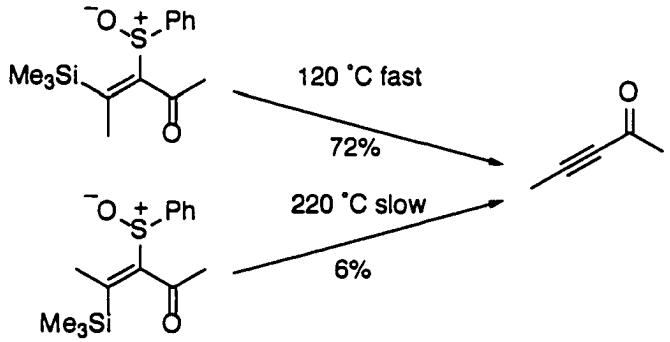
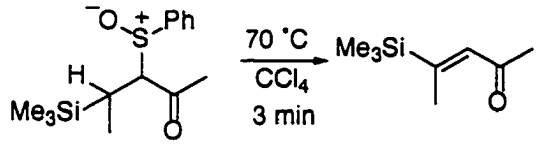



**Figure 15.** Formation of alkyne via loss of β-silyl group




(38)

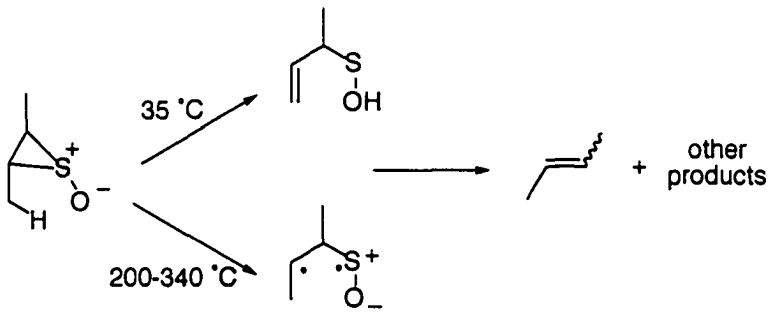
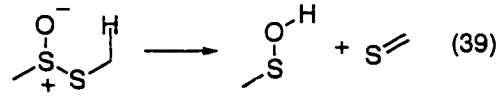



**Figure 16.** Pathways of decomposition of trans-2-butene episulfoxide

Unlike the amine oxides, the intramolecular ring cleavage of sulfoxides has not been extensively investigated. Two studies concerning the decomposition of 2-butene episulfoxides have been undertaken.[58,59] These are presented above in Figure 16. Hartzell and Paige studied the decomposition of cis- and trans-2-butene episulfoxide by injecting in the port of a GC at 150 °C. The cis-2-butene episulfoxide formed a mixture of cis- and trans-2-butene in 89% and 11% yields, respectively, whereas trans-2-butene episulfoxide decomposed to almost an equal amount of cis- and trans-2-butene. The authors suggested a two-step mechanism (E1-like) to account for the loss of stereospecificity. In the second study, Baldwin and co-workers suggested that trans-2-butene episulfoxide decomposes thermally via a sulfenic acid to account for the loss of stereochemistry of the liberated olefins (Figure 16).

**Sulfinyl Derivatives.** Block and co-workers have extensively studied the chemistry of alkyl thiosulfinate esters[60] and this has been reviewed.[61-63] The Ei reaction of methyl methanethiosulfinate (equation 39) affording methanesulfenic acid and thioformaldehyde (as transient intermediates) has been shown to be more facile and produce a complicated reaction mixture compared to the analogous reaction with ethyl methyl sulfoxide.[64] The bond strength of the S-S bond in ethyl methane-thiosulfinate has been measured to be 46 kcal/mol compared to 70 kcal/mol for the S-S bond in dimethyldisulfide.[22] This weaker bond strength of thiosulfinates and the increase acidity of the α-sulfenyl proton accounts for the thiosulfinate's instability and the ease for which it undergoes the Ei reaction, even though sulfinates have been shown to be less basic at oxygen than sulfoxides.[65]



(39)

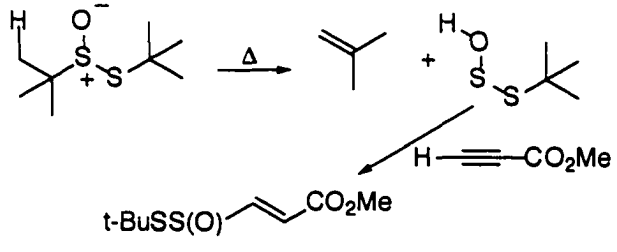
**Table 1**. Thermal stability of alkyl alkanethiosulfinates

| Thiosulfinate | $t_{1/2}$ at 96° (min) |
|---|---|
| MeS(O)SMe | 7 |
| MeS(O)SEt | 11 |
| MeS(O)SPr$^i$ | 32 |
| EtS(O)SMe | 40 |
| n-$C_{12}H_{25}$S(O)S$C_{12}H_{25}$ | 52 |
| $^i$PrS(O)SPr$^i$ | 66 |
| $^t$BuS(O)SBu$^t$ | 148 |
| MeS(O)SBu$^t$ | ~$10^3$ |
| AdS(O)SAd | $10^5$ |

Ad denotes 1-adamantyl

The intermediacy of methanesulfenic acid was confirmed through trapping with alkenes and alkynes. The formation of 1,3,5-trithiane from cracking the polymerized material at 200°C gave evidence for thioformaldehyde.

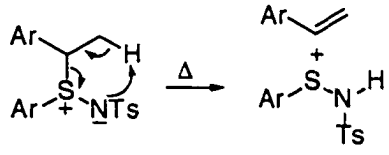
Block found that by blocking the α-sulfenyl position from having hydrogens (i.e. tertiary alkyl groups) the stability of thiosulfinates is dramatically increased Table 1 (shown above).[66,67] The thermolysis of t-butyl t-butanethiolsulfinate afforded t-butanesulfoxylic acid. The existence of tert-butanesulfoxylic acid was provided through trapping experiments with alkynes (equation 40).



(40)

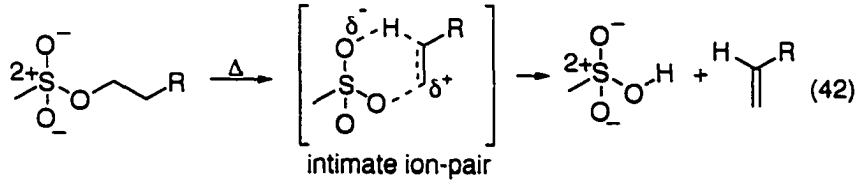
Sulfilimines are the last class of heterocompounds that will be mention regarding an Ei reaction with a five-membered cyclic syn-periplanar transition state.[68] Upon heating, sulfilimines

experience facile elimination, affording stereospecific olefins and sulfenamides (equation 41). Activation barriers for the sulfilimines elimination ($\Delta H^{\ddagger}$ = 20 – 26 kcal/mol) are somewhat lower than in sulfoxides. The authors attributed the ease for which sulfilimines undergo the Ei reaction to the stability of the sulfenamide and basicity of the nitrogen.[68] A primary isotope effect ($k_H/k_D$ = 2.90) has been measured for the case where Ar = phenyl at 25 °C in equation 41 indicative of a bent hydrogen transfer in the transition state since it is below the maximum value (i.e. $k_H/k_D$ = 6 – 7).[68]




(41)

The final Ei reaction that will be reviewed in this chapter is the gas phase pyrolysis of 2-substituted ethyl methanesulfonates.[69] This elimination proceeds through a six-membered transition state producing methanesulfonic acid and an olefin. The pyrolyses, examined in the temperature range of 280 – 360 °C, follow first-order kinetics. Substituents effects were evaulated and the correlation study produced an change in slope in going from electron releasing to electron donating substituents in the plot of log k versus $\sigma^{*}$. This change in slope is indicative of a change in mechanism. Because of this polar effect on the transition state, the author has referred to the transition as an intimate ion-pair (equation 42). The activation barrier is insensitive toward substitution all 17 substituents lie within one kcal/mol of the barrier of 40 kcal/mol.




intimate ion-pair

(42)

**Computational Studies**

The presented reactions and mechanisms from above have demostrated the similiarities between the reaction of amine oxides and sulfoxides. There are also similar structural features if both molecules are written in ylide form. However, since nitrogen is in the first row, we are taught from the beginning that it does not violate the octet rule. Therefore, the N-O bond is well represented as a single bond. In contrast, we are shown exceptions where sulfur can violate the octet rule (e.g. $SF_6$). This exception has created controversy on how to draw the S-O bond in sulfoxides. Mostly for convenience, it seems the literature is populated with the S-O bond in sulfoxides written as a double bond. As shown in the following section there several computational papers concerning exactly how to describe hetroatom oxygen bonds in molecules that can be considered "hypervalent." For purposes of discussion, the heavier congener of amine oxides, namely phosphine oxides, will be compared to sulfoxides (i.e. the bonding of P-O versus the bonding of S-O).

**Hypervalent Molecules**. Computational chemistry of hypervalent molecules presents somewhat of challenge.[70] We define a hypervalent molecule as one that contains an atom that has more than an octet of electrons. The bonding nature of the P-O bond in phosphine oxides has been extensively studied.[71-76] The P-O bond has been characterized as containing one sigma-bond and two pi back-bonds (negative hyperconjugation), a one sigma bond and three pi back-bonds, and three banana bonds (**A**, **B**, and **C**, respectively, in Figure 17). Recently using Atoms in Molecules Theory, Dobado et al. have characterized the P-O bond to be a single highly polarized sigma bond (ylide structure) (Figure 17) in agreement with Schimdt et al.[73]

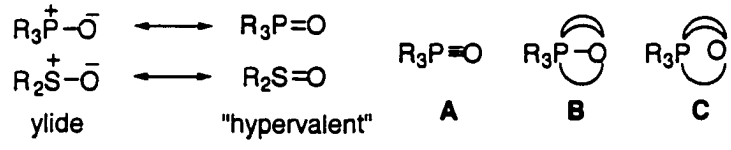


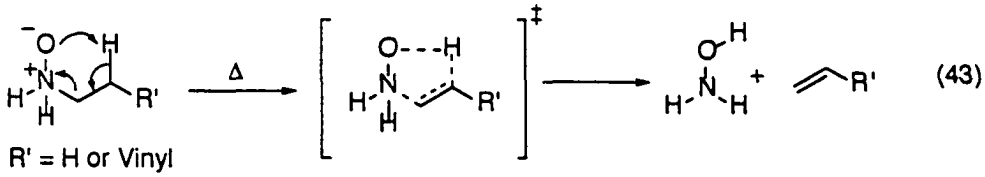

**Figure 17**. Ylide versus hypervalent representation

Cioslowski and Surján have evaluated the nature of sulfoxide bond and have found no evidence for them to be considered hypervalent.[77] In agreement with Cioslowski and Surján, Dobado et al. have again used Atoms in Molecules Theory to investigate the S-O bond in sulfoxides.[78] Again the octet-obeying ylide structure is predicated by theory. In the study B3LYP was compared to MP2

and in all instances MP2 gave structures in better agreement to experimental geometries. The effect of conjugation and aromaticity on the S-O bond was study by Jenks et al.[79] In general the S-O bond was unaffected by conjugation, thus providing further evidence for the ylide structure. With this evidence, the structures of sulfoxides presented in this dissertation are written in ylide form.

**Computations of the Ei reactions**. As presented in the first part of the introduction, the Cope elimination (amine oxides) has been studied thoroughly studied, whereas the Ei reaction of sulfoxides is still under investigation. For comparison, the computational details of the Cope elimination are discussed, followed by the presentation of the sulfoxide elimination. An interlude from Ei reactions presented the effects of the level of theory and basis set size on the stability of isomers for dimethyl sulfoxide (DMSO).

**Amine oxides**. Bach and co-workers have calculated transition state geometries and kinetic isotope effects (KIE) at the MP2/6-31G(d) level and basis.[80] The activation enthalpy was calculated to be 28.2 kcal/mol for the elimination of ethylamine oxide affording ethylene and hydroxylamine (R' = H). This reaction is shown in equation 43. At the MP4SDTQ/6-31G(d)//MP2/6-31G(d) level the activation enthalpy was increased 29.1 kcal/mol. For the elimination of 3-butenylamine oxide producing butadiene and hydroxylamine (R'=vinyl, in equation 43), the barrier was reduced by 2.5 kcal/mol to 25.7 kcal/mol. This value compared closely to the experimental value of 24.3 ± 0.2 kcal/mol for the Ei reaction of 2-phenylethyl-N,N-dimethylamine oxide in DMSO.[35] The primary KIE ($k_H/k_D$ = 3.4) was calculated at 120 °C for 3-butenylamine oxide, in good agreement with the experimental value ($k_H/k_D$ = 3.5 at 110 °C) affording styrene.[41] A secondary KIE was also computed in agreement with experiment (1.079 vs 1.06, respectively).




(43)

In another study on the same Cope elimination reaction, where the ethylamine oxide (R' = H, in equation 43) is thermalized to produce olefins, has been studied computationally by Tronchet and

Komaromi.[81] The computed activation energy was 26.0 kcal/mol at the MP2/6-31(d,p) level and increased to 30.7 at the MP4/6-31G(d,p) level. These energies compare closely with those of Bach. The authors found a 5-membered ring transition state were the hydrogen is transferred to the oxygen with a bond angle (C-H-O) of 148.6° at the MP2/6-31G(d,p) geometry. The activation energies were also calculated at various levels of theory and basis sets (Table 2). There is not an exact experimental value to compare but a general trend can be seen in the activation energies. The HF level of theory gives a high activation energy where as the B3LYP level of theory gives a low activation energy and the MP2 and CCSD(T) levels of theory give fairly consistent numbers in between HF and B3LYP levels of theory, given the differences in the basis set.

**Table 2**. Cope Elimination Reaction Activation Energies ($E_a$) at Various Levels of Theory (R' = H in equation 43)

| Level of Theory/Basis Set | $E_a$ (kcal/mol) |
|---|---|
| HF/6-31G(d,p) | 43.3 |
| MP2/6-31G(d,p) | 26.0 |
| B3LYP/6-31++G(d,p) | 24.3 |
| CCSD(T)(full)/6-311++G(d,p)[a] | 28.8 |

[a]Calculated with MP4(SDQ)(fc)/6-311G(d,p) geometry

Komaromi and Tronchet also computed a mass-weighted intrinsic reaction coordinate (IRC) path for the ethylamine oxide elimination.[81] The IRC showed the hydrogen to be transferred before the C-N bond was broken. Overall, the authors found the Cope elimination to occur in a slightly unsymmetrical concerted fashion.

**Sulfoxides**. To date, there has been one computational study on the specific β-hydrogen syn elimination of sulfoxides.[82] In the study, Jursic compared the syn-elimination of an amine oxide, a sulfoxide, and a phosphine oxide at ab initio and density functional levels of theory using a modest basis set (6-31G(d)). The study revealed the amine oxide elimination to occur with the lowest activation enthalpy. The sulfoxide barrier for elimination was found to be intermediate with the phosphine oxide having the highest activation enthalpy. Hartree-Fock method was shown to give the highest activation enthalpy with MP2 being intermediate and density functional (BLYP) being the lowest. The activation enthalpy for ethyl hydrogen sulfoxide (HS(O)Et) calculated at MP2/6-31G(d) is

32.7 kcal/mol. The author did not report if zero-point corrections were used in computing activation enthalpies.

**Table 3**. Energy (kcal/mol) of Methyl Methanesulfenate Relative to DMSO [a]

| Level of Theory | Basis Set | $CH_3S$-O-$CH_3$ |
|---|---|---|
| B3LYP | 6-31+G(d,p) | -3.6 |
| | 6-311G(2df,p) | 0.8 |
| | 6-311+G(2df,2p) | 3.0 |
| MP2 | 6-311G(d,p) | -4.6 |
| | 6-311G(2df,p) | 3.2 |
| | 6-311+G(2df,2p) | 5.8 |
| | 6-311+G(3df,2p) | 7.1 |
| QCISD(T) | 6-311G(d,p) | -6.3 |
| G2(MP2) | "6-311+G(3df,2p)" | 5.3 |

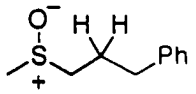
[a]See reference 83

**Sulfoxide Stability**. In another computational study comparing isomers of $C_2H_6SO$, Turecek found that the energy of methyl methanesulfenate ($CH_3S$-O-$CH_3$) varied tremendously compared to dimethyl sulfoxide (DMSO) depending on basis set size (Table 3).[83] At smaller basis set size (6-31+G(d,p)), DMSO is predicted to be less stable than the sulfenate ester by at least 3.6 kcal/mol at the lowest level of theory (B3LYP). In addition, the highest level of theory (QCISD(T)) used incorrectly predicts the energy of DMSO with the 6-311G(d,p) basis set. Therefore, the level of theory is not the affecting the energy since all levels of theory give basically the same answer with similar basis set size (Table 3). Thus, the stability of the sulfoxide must be underestimated with the smaller basis set. Increasing the basis set by the addition of one more set of d polarization functions and set of f polarization functions predicts DMSO to be more stable than the corresponding sulfenate ester at both B3LYP and MP2 levels of theory. Accordingly, the addition of two more sets of d functions, one set of f functions, and a set of p functions increases the stability of DMSO over methyl methanesulenate even more. DMSO is predicted to be 7 kcal/mol more stable than the sulfenate ester at the MP2/6-311+G(3df,2p) level and basis set. The best calculation of energy used in the study, the G2(MP2) calculation which utilizes the 6-311+G(3df,2p) basis set, predicts DMSO to be

more stable by 5.3 kcal/mol. Therefore the addition of extra d functions looks to be important in getting the energy of sulfoxides right relative to sulfenate esters. This will provide incentive to be careful in comparing energies of sulfoxides to the energy of sulfenic acids (RSOH) that are produced in the elimination reaction of sulfoxides.

**Current Investigation**

In this chapter, we present the thermolysis of several sulfoxides and derivatives. From the experimental determination of the gas-phase activation parameters using a pulsed stirred-flow apparatus, we compare the experimental activation barriers with computed values of model compounds. The model compounds aid in computationally clarifying and quantifying the mechanistic hypotheses of the sulfoxide Ei reaction. An example of a sulfoxide studied is shown below. The molecule is color coded to illustrate the computational molecule. The black part of the molecule is the computational analog and the red section is the insulated phenyl group for ease of detection in the experiment. Below are presented results from gas-phase activation data, kinetic isotope effects, and ab initio computations that all strongly support the concerted elimination of sulfoxides and derivatives.

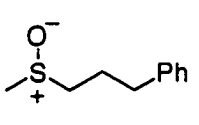



# Results

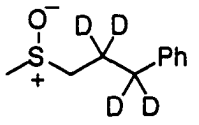
We have studied the thermolysis of several sulfoxides and derivatives using a pulsed stirred-flow apparatus, which allows the reaction to be carried out in the gas phase in a bath of He.[84] From the rate constants collected using the stirred-flow apparatus, we are able to obtain Arrhenius plots which give the gas-phase activation parameters. Each compound was chosen to have only one side with β-hydrogens available for the elimination to occur as well as an additional phenyl group insulated from the reaction site for ease of product detection.

Compounds **1** - **3** were chosen to examine the effect of methyl, vinyl, and phenyl substituents on the elimination kinetics. Sulfoxides **1a** and **1b** were prepared in order to evaluate the isotope effect under stirred-flow conditions. Sulfinyl derivatives **4** and **5** were going to be used to

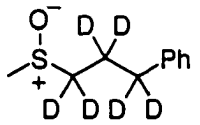
investigate the effects of amino and trifluoro groups on the elimination kinetics, but due to difficulties with either the stirred-flow instrument or compound preparation the activation parameters could not be determined. Sulfoxides **6, 6a**, and **6b** were chosen to investigate the kinetics and transition state for the formation of an alkyne. In order to gain insight in the elimination reaction of sulfinic esters, sulfinic ester **7** was prepared.



**1**



**1a**



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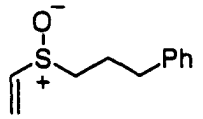
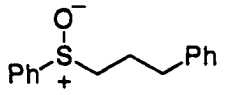
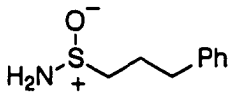


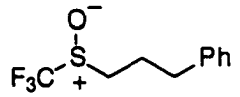
**2**



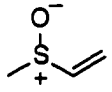
**3**



**4**



**5**



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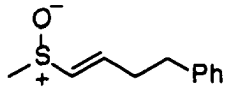
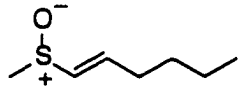
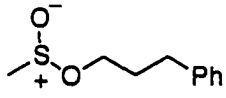


**6a**



**6b**



**7**

Utilizing the activation parameters from the stirred-flow reactor, we compared the gas-phase computed values to the gas-phase experiments to gain insight into which level of theory and basis set size is needed to accurately and to reliably reproduce the elimination energetics. The nature of the transition states (TS) in the Ei reaction were probed using the complete active space self-consistant

field (CASSCF) method. To gain insight into the symmetric nature of the elimination reaction path, intrinsic reaction coordinate (IRC) calculations were carried out to connect the TS, starting material, and products on certain sulfoxides and derivatives.

Once the level of theory and basis set is determined to accurately reproduce experimental energetics, several other sulfoxides can be calculated in the Ei regime. Since experiments were only suitable for certain sulfoxides and derivatives, calculations allowed access to energetics for many more compounds. A series of sulfoxides were utilized to observe computationally the effects of substituents, the effects of steric crowding, and the effect of acidity at the β-hydrogen on the Ei reaction. Finally, the Ei reaction energetics for sulfinyl derivatives were computed.

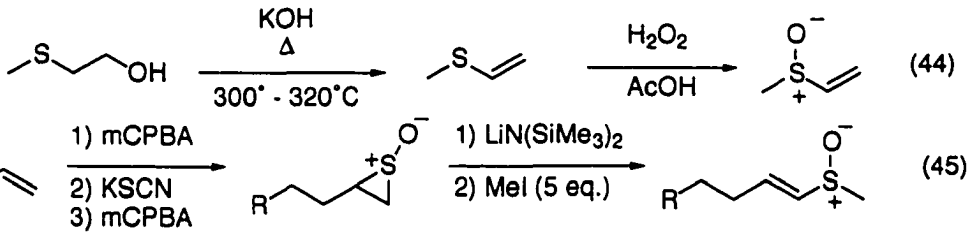
## Experimental

**Compound Preparation**. Sulfoxides **1** - **3** were prepared by oxidation of the corresponding sulfides, which were obtained by thiolate displacement of an alkyl halide. Sulfoxides **1a** and **1b** were prepared from reduction of ethyl phenylpropiolate with $D_2$ to give ethy 2,2,3,3-tetradeutero-3-phenylpropionate. This ester was then reduced with either $LiAlH_4$ or $LiAlD_4$ to provide the 2,2,3,3-$d_4$- or 2,2,3,3,4,4-$d_6$-3-phenylpropanol, respectively. These alcohols were then converted to their corresponding tosylates and the tosylates were displaced by methane thiolate. Finally, the sulfides were oxidized to the corresponding sulfoxides. Sulfinamide **4** was prepared by adding the corresponding sulfinyl chloride to liquid ammonia. Preparation of 3-phenylpropyl methanesulfinate **7** was straight forward from the corresponding alcohol and methanesulfinyl chloride. Details are provided in the Experimental section.

Several unsuccessful attempts were made to prepare trifluoromethyl sulfoxide **5**. 3-phenylpropyl trifluoromethyl sulfide was prepared from the corresponding disulfide and a trifluoromethyl anion equivalent, but oxidation by several different methods did not provide the expected sulfoxide. Di-(3-phenylpropyl) sulfoxide was isolated in the case of m-CPBA oxidation.

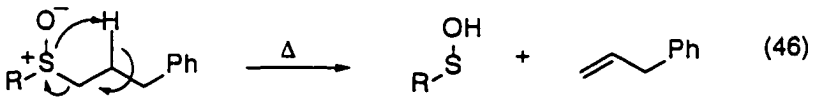
Synthesis of **6** deserves a special note. Before coming across a "sledge hammer" preparation of methyl vinyl sulfide, several "elegant" syntheses were attempted and all were unsuccessful. Some of the attempts included turning the alcohol functionallity of 2-(methylthio)ethanol into a better leaving group (e.g. tosylate and mesylate) with both the sulfide and

the corresponding sulfoxide followed by a base initiated elimination. The Schwan and Refvik procedure[85] was attempted where ethylene S-oxide is deprotonated by lithium hexamethyldisilazide and the anion then trapped with methyl iodide. All of the "elegant" sytheses lead to polymerized material as shown from broadening of peaks in the nmr spectra and isolation of target sulfoxide **6** was never achieved. A reference in a Chinese journal described a simple, if inelegant, preparation of **6** (equation 44).[86] The authors devoted only one sentence for the hot KOH step; in our hands, this step produced methyl vinyl sulfide in almost quantitative yield once efficient trapping of the sulfide (a gas) was achieved (see experimental for complete details). The authors of the paper however had worked out the oxidation step and this step provided **6** in greater than 90 percent yield after careful extraction. Unsaturated sulfoxides **6a** and **6b** were prepared by the Schwan and Refvik method (equation 45).[85]




**Thermolysis**. Unless otherwise discussed pulsed stirred-flow thermolysis of the sulfoxide cleanly produced the expected olefin. Formation of the sulfenic acids is inferred, since none of them survived GC analysis. Useful data were only obtainable when activation enthalpies were about 30 kcal/mol or greater.

Thermolysis of sulfoxides **1-3** produced allyl benzene as a common olefin (equation 46). Sulfoxide **3** reacted at too low of a temperature to obtain reliable activation parameters. Sulfinamide **4** did not survive the chromatography to give accurate measurement of the peak areas. Activation parameters are shown in Table 4 for sulfoxides **1** and **2**.



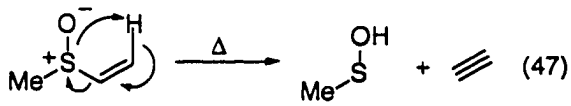

R = Me (**1**), Vinyl (**2**), Phenyl (**3**)

**Table 4.** Activation parameters for the pulsed stirred-flow thermolysis of **1**, **2**, **6**, and **7**

| Sulfoxide | **1** | **2** | **6** | **7** |
|---|---|---|---|---|
| Temp. (°C) | 240-300 | 225-270 | 340-400 | 270-340 |
| log(A) (1/sec) | 12.5 ± 0.3 | 12.1 ± 0.8 | 13.1 ± 0.3 | 10.9 ± 0.2 |
| $E_a$ (kcal/mol) | 34.0 ± 0.9 | 30.8 ± 0.8 | 42.9 ± 0.8 | 35.7 ± 0.6 |
| $\Delta H^{\ddagger}$ (kcal/mol) | 32.9 ± 0.9 | 29.8 ± 0.8 | 41.6 ± 0.8 | 34.6 ± 0.6 |
| $\Delta S^{\ddagger}$(cal/mol K) | -4.5 ± 0.8 | -6.5 ± 0.8 | -2.1 ± 1.2 | -12.1 ± 1.0 |

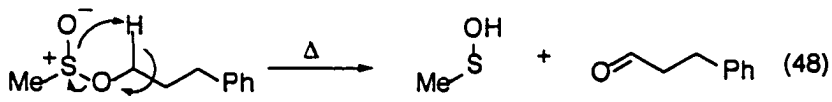
Errors are expressed as two standard deviations of the least squares fit.

Sulfoxide **6** eliminated to form acetylene (equation 47). Activation parameters are shown in Table 4. Thermolyses of methyl (E)-4-phenyl-1-enyl sulfoxide (**6a**) and methyl hex-1-enyl sulfoxide (**6b**) were found to produce 4-phenyl-1-butyne and 1-hexyne, respectively. However, both thermolyses produced several other products. To gain insight into some of the other products formed, the flow pyrolysis of **6a** was carried out. Along with the alkyne, the other major products were found to be isomers of **6a** as detected from analyzing the flow pyrolysis mixture via GC/MS. Since eliminations of **6a** and **6b** produced several products, the kinetics were complicated and activation parameters for alkyne production could not be evaluated. Therefore, the parent sulfoxide **6** was used and good data were obtained.



(47)

Elimination by sulfinic ester **7** gave 3-phenylpropanal (equation 48). Activation parameters are shown in Table 4. A plot of the logarithmic forms of the Arrhenius equation and the Eyring equation is shown for ester **7** in Figure 18. This is a typical plot for all of the molecules thermolyzed. Arrhenius and Eyring plots for **1**, **2**, **6**, and **7** are shown in Appendix 1.



(48)

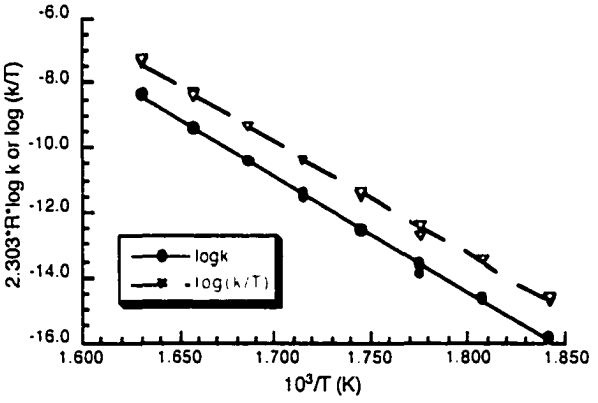



**Figure 18**. Arrhenius and Eyring plots of 3-phenylpropyl methanesulfinate (270° – 340°C). Data points are from three runs at each temperature.

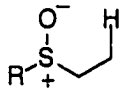
**Isotope Effects**. The kinetic isotope effect (KIE) for **1** vs. **1a** and **1b** was evaluated by successive injections in the SFR of **1**, **1a**, and **1b** on the same day using the reactor cell to insure accuracy. The $k_H/k_D$ was determined over the temperature range of 230-280 °C with value as the average of three runs at ten degree increments. The KIEs were averaged over the temperature range because the difference over the temperature range was less than the scatter. The $k_H/k_D$ for **1** vs. **1a** was found to be 2.5 ± 0.3. The $k_H/k_D$ for **1** vs. **1b** was found to be 2.8 ± 0.9 averaged over the temperature range. The $k_{D4}/k_{D6}$ for **1a** vs. **1b** was found to be 1.26 ± 0.16 averaged over the temperature range. Errors stated here are two standard deviations from mean.

## Computational

Eight groups of sulfoxides and derivatives were computed, many compounds are compared to experimental activation parameters that were determined by our group or known in the literature. Activation enthalpies ($\Delta H^{\ddagger}$) are calculated from the difference in energy between the transition state and the starting sulfoxide. Heats of reaction ($\Delta H_{rxn}$) are computed by the difference in energy between the products (sulfenic acid and olefin) and the starting sulfoxide.

Group 1 sulfoxides and **17** and **18** were used in a level of theory study. Sulfoxide **8** was used in a basis set study. Once the levels of theory and basis set was found to correctly reproduce the activation parameters the other groups of compounds were computed. The nature of the

transition state (TS) was probed using the complete active space self-consistant field (CASSCF) method on sulfoxides **8** – **11** and **18**. Intrinsic reaction coordinate (IRC) calculations were carried out on compounds **8**, **17**, **18**, **32** – **35** to connect the TS, starting material, and products.

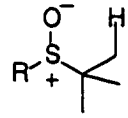


Group 1

R = $CH_3$ (**8**), $C_2H_3$ (**9**), Ph (**10**), $CF_3$ (**11**)

Group 2

R = H (**12**), F (**13**), $NH_2$ (**14**)

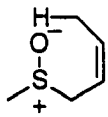


Group 3

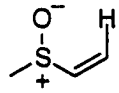
R = $CH_3$ (**15**), t-Bu (**16**)

Sulfur substituent effects on the activation barrier were detected from computing Group 1 and 2 sulfoxides. The effect of a t-butyl substituent at sulfur for the elimination of ethylene was shown for Group 3 substrates. The sulfoxides in Group 4 investigated formation of a 7-membered ring transition state (**17**), production of acetylene (**18**), and production of allene (**19**). Group 5 sulfoxides served to discover elimination barrier in forming α,β-unsaturated ketones and aldehydes. Is endo or exo elimination favored and which ring size has the lowest activation barrier were questions that were answered with the Group 6 compounds. Sulfinyl derivatives in Group 7 calculated the barrier for formation of an aldehyde (**32** and **33**), an imine (**34**), and a thioaldehyde (**35**). Group 8, sulfoxide **36**, evaluated the formation of an endo or exo alkene to form an unsaturated carbonyl as function of diastereromers.

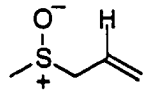
Group 4



**17**

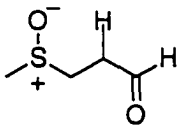


**18**

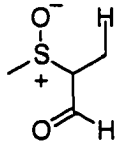


**19**

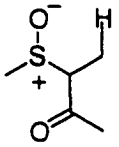
Group 5



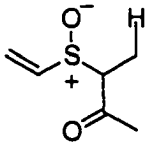
**20**



**21**

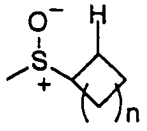


**22**

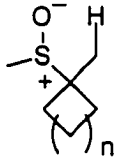


**23**

Group 6

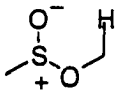


n = 0 (**24**), 1 (**25**), 2 (**26**), 3 (**27**)

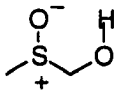


n = 0 (**28**), 1 (**29**), 2 (**30**), 3 (**31**)

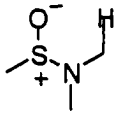
Group 7



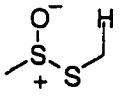
**32**



**33**

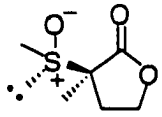


**34**

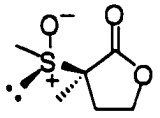


**35**

Group 8



**(3R, SR) 36**



**(3R, SS) 36**

**Methodology**

**Level-of-theory study**. For the level-of-theory study on Group 1 sulfoxides and **17** and **18**, the ab initio methods employed were Hartree-Fock theory (HF), Moller-Plesset second order perturbation theory (MP2), and Coupled-Cluster singles, doubles, with triples treated perturbationally (CCSD(T)).[87] The hybrid density-functional method of Becke's three parameter exchange functional with Lee, Yang, and Parr's correlation functional[88-90] (B3LYP) was also utilized. Optimizations were carried out at each level of theory, except CCSD(T) where the MP2/6-31G(d,p) geometries were used. All of the level-of-theory calculations were carried out using the 6-31G(d,p) basis set. Zero-

point energy (unscaled) corrections are included as computed for each level of theory unless otherwise noted. The calculated activation enthalpies and heats of reaction are reported in Tables 5 and 6, respectively.

**Table 5**. Activation Enthalpies (kcal/mol) for Sulfoxides **8**, **9**, **10**, **11**, **17**, and **18**.

| Theory | **8** | **9** | **10** | **11** | **17** | **18** |
|---|---|---|---|---|---|---|
| HF | 44.0 | 43.5 | 42.7 | 41.2 | 56.0 | 50.1 |
| MP2 | 28.9 | 28.6 | 28.5 | 27.4 | 53.7 | 37.9 |
| CCSD(T)[a] | 29.6 | 29.3 | 29.2 | 27.6 | 49.4 | 39.4 |
| B3LYP | 23.5 | 22.5 | 22.3 | 21.9 | 41.4 | 34.4 |

[a]The MP2 level zero-point correction (ZPE) was used to estimate the ZPE correction at the CCSD(T) level. All values otherwise were optimized with a 6-31G(d,p) basis set.

**Table 6**. Heats of Reaction (kcal/mol) for Sulfoxides **8**, **9**, **10**, **11**, **17**, and **18**.

| Theory | **8** | **9** | **10** | **11** | **17** | **18** |
|---|---|---|---|---|---|---|
| HF | 0.4 | -2.1 | 0.5 | -3.5 | -5.2 | 15.0 |
| MP2 | 12.8 | 9.6 | 14.5 | 9.8 | 16.6 | 20.4 |
| CCSD(T)[a] | 8.5 | 7.8 | 9.5 | 5.0 | 6.3 | 19.5 |
| B3LYP | 9.0 | 8.4 | 8.5 | 6.8 | 6.4 | 22.9 |
| Estimated[b] | 21 | | 22 | | | 31 |

[a]The MP2 level zero-point correction (ZPE) was used to estimate the ZPE correction at the CCSD(T) level. All values otherwise were optimized with a 6-31G(d,p) basis set. [b]$\Delta H_f^\circ$ estimated from a Benson calculation for parent sulfoxide, G2 calculation for methanesulfenic acid, and experimental value for alkene/yne and benzenesulfenic acid.

From the calculated activation enthalpies (Table 5), it is shown that HF theory predicts a barrier much higher than the other levels of theory. The density functional (B3LYP) theory calculated the lowest activation enthalpy, with MP2 and CCSD(T) theories producing similar values for all but for 2-butenyl methyl sulfoxide **17**. This discrepancy is unclear at this time. Comparison of experimental activation enthalpies for sulfoxides **1** and **2** with computed enthalpies for **8** and **9** produced values somewhat close to each other. The experimental trend (Table 4) that was observed in going from

sulfoxide **1** to **2** was a 3.1 kcal/mol lowering in $\Delta H^{\ddagger}$. Albeit a small trend, this is not reproduced at any of the levels of theory with the 6-31G(d,p) basis set. In fact sulfoxides **8** – **11** all are giving similar values for the $\Delta H^{\ddagger}$. Only methyl vinyl sulfoxide **18** reproduced the experimental value (41.6 kcal/mol) within 2 kcal/mol at the CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p) level.

In observation of the heats of reaction (Table 6), no obvious trends were apparent between sulfoxides. The trend illustrated between levels of theory, is HF theory clearly predicts the reaction in the wrong direction (i.e. exothermic not endothermic). The other levels of theory at least predict the reaction to be endothermic. The heats of reactions were for estimated for **8**, **10**, and **18** using Benson-type calculations for $\Delta H_f^{\circ}$ of sulfoxide, G2 determined $\Delta H_f^{\circ}$ for methanesulfenic acid, and experimentally determined $\Delta H_f^{\circ}$ for alkene/yne. The estimated $\Delta H_{rxn}$ for **8**, **10**, and **18** were 21, 22, and 31 kcal/mol, respectively. No $\Delta H_{rxn}$ calculated at any of the levels of theory were close to these values (Table 6). These results suggested that the stability of sulfoxide is underestimated as compared to the sulfenic acid by the basis set size, as was observed by Turecek for DMSO versus MeS-O-Me.[83]

**Basis set study**. Since increasing the level of theory with the 6-31G(d,p) basis set does not reproduce the experimental trend in the $\Delta H^{\ddagger}$ and there is no agreement in the $\Delta H_{rxn}$, the molecules must not be represented completely by the size of the basis set. Therefore, a basis set study was conducted. Since the MP2 level of theory gave similar $\Delta H^{\ddagger}$ values as compared to CCSD(T) level of theory, it was decided to use the much cheaper MP2 level of theory for the basis set study. The effect of the basis set size on $\Delta H^{\ddagger}$ and $\Delta H_{rxn}$ are shown in Table 7 with both Pople-type (e.g. 6-31G(d,p)) and Dunning's correlated consistent basis sets (e.g. cc-PVDZ).

From Table 7, the basis sets are arranged from a small number of basis functions to a large number of basis functions within a given category, i.e. the double-zeta split-valence basis set (6-31G). Comparing to MP2/6-31G(d,p), increasing the basis size by adding diffuse sp functions on the heavy atoms has little effect of either $\Delta H^{\ddagger}$ or $\Delta H_{rxn}$. The addition of the second set of d functions on the heavy atoms produces an increase of 3.2 kcal/mol on the $\Delta H_{rxn}$ but has no effect on $\Delta H^{\ddagger}$. Adding the set of f functions on the heavy atoms has a 7.2 kcal/mol increase on the $\Delta H_{rxn}$ and 1.0 kcal/mol increase on $\Delta H^{\ddagger}$. No effect was shown by the addition of the second set of p functions on hydrogen. Finally, with

**Table 7**. Basis Set Evaluation at MP2 level on the Elimination Reaction for Sulfoxide **8**.[a]

| Basis Set Size | # of basis functions on **8** | $\Delta H^{\ddagger}$ (kcal/mol)[b] | $\Delta H_{rxn}$ (kcal/mol)[b] |
|---|---|---|---|
| 6-31G(d,p) | 119 | 32.9 | 16.6 |
| 6-31+G(d,p) | 139 | 33.4 | 16.5 |
| 6-31++G(d,p) | 147 | 33.2 | 16.7 |
| 6-31G(2d,p) | 149 | 32.7 | 19.9 |
| 6-31G(2df,p) | 199 | 33.9 | 23.8 |
| 6-31G(2df,2p) | 223 | 33.8 | 23.9 |
| 6-31G(3df,2p) | 253 | 36.3 | 27.3 |
| 6-31+G(3df,2p) | 274 | 36.3 | 26.3 |
| 6-311G(d,p) | 151 | 29.8 | 18.1 |
| 6-311++G(d,p) | 179 | 31.2 | 15.6 |
| 6-311G(3d,p) | 211 | 33.0 | |
| 6-311G(2df,p) | 231 | 33.1 | 23.9 |
| 6-311G(3d,2p) | 235 | 32.7 | |
| 6-311G(2df,2p) | 255 | 33.3 | 23.4 |
| 6-311+G(3df,2p) | 305 | 36.3 | 26.3 |
| cc-PVDZ | 119 | 25.1 | |
| aug-cc-PVDZ | 201 | 27.4 | |
| cc-PVTZ | 299 | 31.7 | |
| aug-cc-PVTZ | 479 | 32.4 | |
| Experiment | | 33 | 21 |

[a]Single point calculations at various basis sets on the optimized MP2/6-31G(d,p) geometry. [b]Note: No ZPEs included in energies. ZPE corrections for $\Delta H^{\ddagger}$ = 3.0 kcal/mol and for $\Delta H_{rxn}$ = 3.7 kcal/mol

the addition of the third set of d functions the energies (both $\Delta H^{\ddagger}$ and $\Delta H_{rxn}$) start to converge, indicating comparable quality description of the sulfoxide, the TS, and the sulfenic acid.

With triple zeta split-valence basis set (6-311G), the same trends are apparent as with the trends of the double zeta basis set (Table 7). A couple of further tests were done with the triple zeta basis set. The addition of three sets of d polarization functions on the heavy atoms without the addition of the f polarization functions showed only a modest improvement on the $\Delta H^{\ddagger}$. The addition of the second set of p functions on hydrogen without the f functions or diffuse sp functions on the

heavy atoms also produce a lower $\Delta H^{\ddagger}$ value than with the f and diffuse sp functions, i.e. comparison of 6-311G(3d,2p) to 6-311+G(3df,2p).

Dunning's correlated-consistent basis sets were also tested on $\Delta H^{\ddagger}$. They converged rather slowly and do not reproduce the energetics until utilizing 479 basis functions (aug-cc-PVTZ) which is still going to underestimate the barrier by approximately 3 to 4 kcal/mol once zero-point energy corrections are included. Though attractive in principle, the correlated-consistent basis sets thus proved impractical, since aug-cc-PV5Z bases would simply be too large to handle.

Experimentally, ethyl methyl sulfoxide **8** and ethyl vinyl sulfoxide **9** have $\Delta H^{\ddagger}$ values of 32.9 and 29.8 kcal/mol, i.e. a difference of 3.1 kcal/mol. This difference is not reproduced by MP2/6-31G(d,p) though the absolute values, once ZPEs are added, are within a few kcal/mol. However, the difference is reproduced fairly well beginning with the 6-31+G(3df,2p) basis set (Table 7). This result was used as precedent to test B3LYP at the larger basis sets. The values in Table 8 show that the experimental trend between **8** and **9** is reproduced at this level of theory but that the absolute values remain too low with B3LYP, even with the larger basis set.

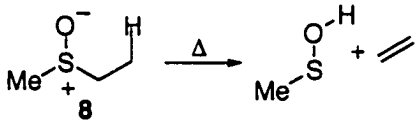
**Table 8**. Activation Barriers[a] at MP2/6-31+G(3df,2p) for Sulfoxides **8**, **9**, **10**, **11**, **17** and **18**.

| Theory | **8** | **9** | **10** | **11** | **17** | **18** |
|---|---|---|---|---|---|---|
| MP2[b] | 32.3 | 30.4 | 30.6 | 30.7 | 47.8 | 40.3 |
| B3LYP[c] | 29.2 | 26.9 | 26.6 | 27.9 | ----- | 40.0 |

[a]Values are in kcal/mol. [b]Single point calculations on the optimized MP2/6-31G(d,p) geometry. ZPEs taken from MP2/6-31G(d,p) geometry. [c]ZPEs taken from the optimized B3LYP/6-31G(d,p) geometry.

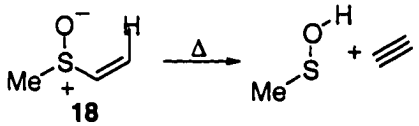
After discovering that the 6-31G(3df,2p) and 6-31+G(3df,2p) basis sets are considered unbalanced from under representing the functions on core orbitals and over representing the functions on valence orbitals,[91,92] it was decided to use the better balanced triple zeta basis set (6-311+G(3df,2p)). The Pople triple zeta basis set, MP2/6-311+G(3df,2p), was tested to compute reaction energetics at the MP2/6-31G(d,p) geometries. Two sulfoxides **8** and **18** were optimized at the MP2/6-311+G(3df,2p) level to see the effects on the energetics and geometries of optimizing rather than using MP2/6-31G(d,p) geometries. The energetics on the elimination of **8** and **18** did not produce substantial changes in either $\Delta H^{\ddagger}$ and $\Delta H_{rxn}$. The $\Delta H^{\ddagger}$ for **8** and **18** at the MP2/6-

311+G(3df,2p) is 32.6 kcal/mol and 41.0 kcal/mol, respectively, thus giving changes from the MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) level of 0.3 and 0.7 kcal/mol for **8** and **18** in the $\Delta H^{\ddagger}$, respectively. The $\Delta H_{rxn}$ for **8** and **18** optimized at MP2/6-311+G(3df,2p) is 23.2 kcal/mol and 29.7 kcal/mol, respectively, thus giving changes from the MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) level of 0.6 and 1.0 kcal/mol for **8** and **18** in the $\Delta H_{rxn}$, respectively. The $\Delta H_{rxn}$ values computed using MP2/6-311+G(3df,2p) is now in good agreement with the estimated $\Delta H_{rxn}$ values for **8** and **18** ($\Delta H_{rxn}$ = 21 and 31 kcal/mol, respectively). These changes, with the optimizations at MP2/6-311+G(3df,2p), in energy were not judged to be substantial enough to justify the computer time. This supports the single point calculations on the smaller basis set geometry at the MP2 level of theory.



**8**

At MP2/6-311+G(3df,2p):
$\Delta H^{\ddagger}$ = 32.6 kcal/mol
$\Delta H_{rxn}$ = 23.2 kcal/mol



**18**

At MP2/6-311+G(3df,2p):
$\Delta H^{\ddagger}$ = 41.0 kcal/mol
$\Delta H_{rxn}$ = 29.7 kcal/mol

**Geometry Comparision**. Geometries for ethyl methyl sulfoxide (**8**) and its TS (**8 TS**) and methyl vinyl sulfoxide (**18**) and its TS (**18 TS**) are shown in Figure 19 and 20, respectively. These geometries reflect the general trend in geometry changes as a function of level of theory and basis set size. The geometries for all the sulfoxides and sulfinyl derivatives are depicted in Appendix 2, Figures 1 – 29. Geometries for the sulfenic acids are shown in Appendix 3. The structures of the alkenes are shown in Appendix 4. For comparison of bond lengths, dimethyl sulfoxide (DMSO) experimental bond lengths, as determined from microwave spectroscopy, are C-S bond (1.808 Å) and S-O (1.485 Å).[93] In sulfoxide **8**, it can be seen that HF/6-31G(d,p) and MP2/6-311+G(3df,2p) give very similar bond lengths for both the C-S and S-O, 1.80 Å and 1.49 Å, respectively. Those bond distances are in very good agreement with the experimental bond lengths of DMSO, where as MP2/6-31G(d,p) and Becke3LYP/6-31G(d,p) overestimate the bond lengths. The result that HF/6-31G(d,p) bond lengths are very good would appear to be due to fortuitous cancellation of errors from basis set (too long) and level of theory (too short). All theories and basis sets tend to give accurate C-H bonds and C-C bonds. These trends are present in all sulfoxides computed as seen in Figure 20 with **18**.

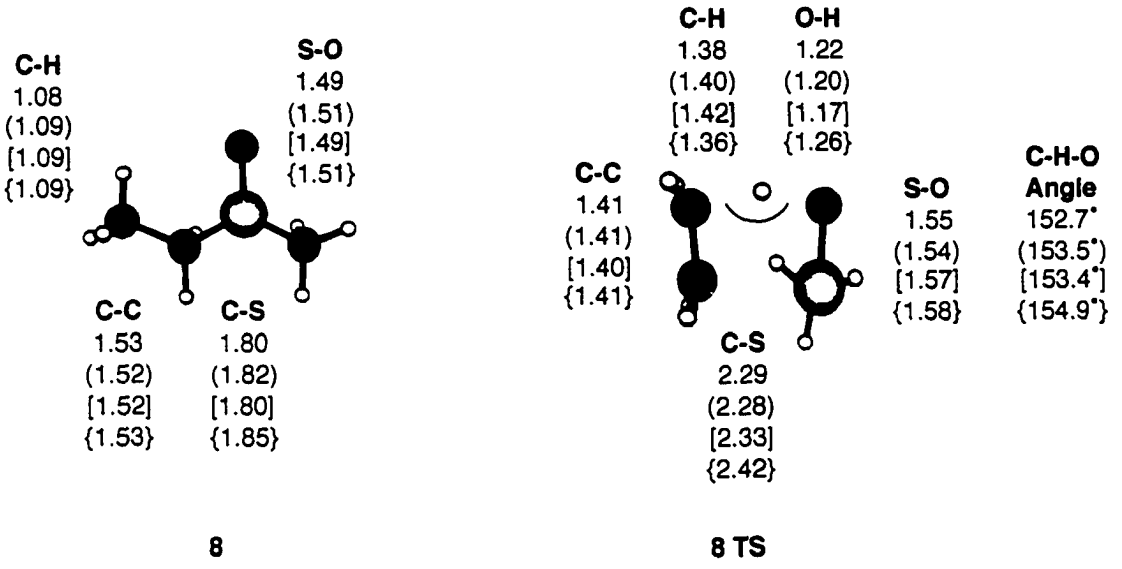



**Figure 19**. Geometry of ethyl methyl sulfoxide, **8**, and its transition state, **8 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), (MP2/6-31G(d,p)), [MP2/6-311+G(3df,2p)], and {Becke3LYP/6-31G(d,p)}, respectively.

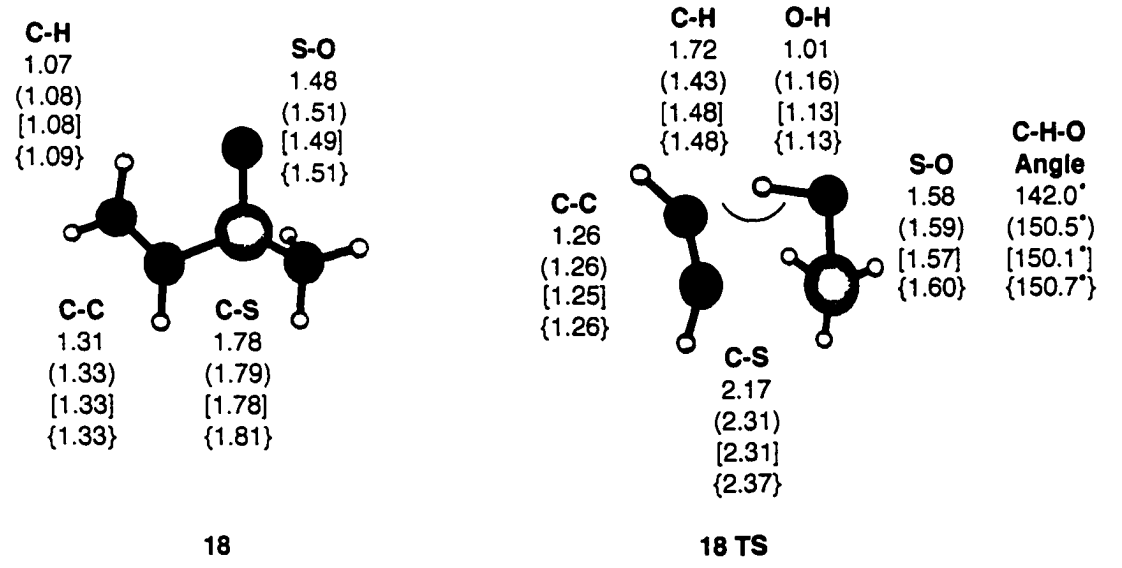



**Figure 20**. Geometry of methyl vinyl sulfoxide, **18**, and its transition state, **18 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), (MP2/6-31G(d,p)), [MP2/6-311+G(3df,2p)], and {Becke3LYP/6-31G(d,p)}, respectively.

Comparing the transition state geometries to the starting material geometries a general trend will appear. In the transition state, the C-S distance is lengthened to over 2.1 Å. The C-C bond is shortened showing the formation of the olefin. The C-H bond is lengthened as the proton is transferred to the oxygen. The partial O-H bond formation can be seen as it is within 1.3 Å in all cases. The S-O bond is always lengthened about 0.1 Å in the TS. The H transfer angle (C-H-O) is always about 154°. Some discrepancies will be noted in the Discussion section.

A general trend in the level of theory used is that B3LYP/6-31G(d,p) give slightly longer S-O and S-C bonds. Figure 20 shows one exception to the general uniformity of structures where HF/6-31G(d,p) give a dramatically different structure that the other theories for the transition state. From the equalilibrium geometry comparison, it is seen that the MP2/6-311+G(3df,2p) level gives the best geometries and in principle this should apply to the TS. Since it is very expensive to optimize structures of size at MP2/6-311+G(3df,2p), and the geometries are fairly similar to the MP2/6-31G(d,p) all of the rest of the structures were only optimized at the HF/6-31G(d,p) and MP2/6-31G(d,p). Since the energetics for the B3LYP/6-31G(d,p) are always low and the structures are slightly different from the MP2 geometries this method was abandoned for the rest of the groups.

From the methodology study, the highest quality affordable method was MP2 level of theory. The basis set, although being the largest Pople basis set studied, produced the most accurate energetics and its use was not compromised. For the rest of this chapter the energetics are reported at the MP2/6-311+G(3df,2p)// MP2/6-31G(d,p) level of theory and basis set. Before moving on to computed results for all of the molecules, the results from the CASSCF calculations and the IRC methods for the molecules of Group 1 and **17** and **18** are presented.

**CASSCF Computations.**[94] In order to probe the nature of the transition states for diradical character, complete active space self-consistent field (CASSCF) calculations were carried out on **8 TS – 11 TS** and **18 TS**. This method uses a full-optimized reaction space (FORS) to allow full mixing of active electrons with all active orbitals. The first step to run CASSCF calculations is selecting an active space. An active space is composed of doubly occupied orbitals and unoccupied orbitals for the nominally close shell cases, but can have singularly occupied orbitals when looking at excited states, radicals, and other reactive intermediates.

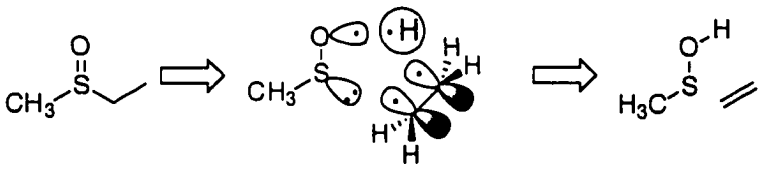


**Figure 21.** Selection of the active space for CASSCF calculation of **8 TS** of 6 electrons in 5 orbitals

RHF methods with the Boys localization[95] protocol were used to gain good starting orbitals for the active space. For ethyl methyl sulfoxide **8 TS** and trifluoromethyl ethyl sulfoxide **11 TS**, the active space contained 6 electrons in 5 orbitals, [6,5], (Figure 21). The input orbitals in the transition state correlated to the C-S $\sigma$ and $\sigma^*$ orbitals, the C-H $\sigma$ and $\sigma^*$ orbitals, and a lone pair on O in the starting material. The correlation to the product was to the C-C $\pi$ and $\pi^*$ orbitals, O-H $\sigma$ and $\sigma^*$ orbitals, and a lone pair on sulfur. For ethyl vinyl sulfoxide **9 TS**, ethyl phenyl sulfoxide **10 TS,** and methyl vinyl sulfoxide **18 TS**, the active space contained 8 electrons in 7 orbitals. The input orbitals were the same as for **8 TS** and **11 TS**, except for extra C-C $\pi$ and $\pi^*$ orbitals in the starting materials for **9** and **10**. The correlation to the product was the same as **8 TS** and **11 TS** except for **18 TS** where extra C-C $\pi$ and $\pi^*$ orbitals were included for the formation of acetylene.

**Table 9**. Natural Orbital Occupation Numbers (NOONs) for **8 TS** – **11 TS** and **18 TS**[a]

| **8 TS** | **9 TS** | **10 TS** | **11 TS** | **18 TS** |
|---|---|---|---|---|
| [6,5] | [8,7] | [8,7] | [6,5] | [8,7] |
| 1.969 | 1.911 | 1.977 | 1.970 | 1.933 |
| 1.971 | 1.934 | 1.934 | 1.967 | 1.981 |
| 1.998 | 1.977 | 1.992 | 1.998 | 1.991 |
| 0.030 | 1.991 | 1.956 | 0.031 | 1.946 |
| 0.033 | 0.071 | 0.024 | 0.035 | 0.060 |
| | 0.024 | 0.043 | | 0.068 |
| | 0.092 | 0.074 | | 0.020 |

[a]See Appendix 2 for transitions states at MP2/6-31G(d,p): ethyl methyl sulfoxide **8 TS**, ethyl vinyl sulfoxide **9 TS**, ethyl phenyl sulfoxide **10 TS**, ethyl trifluromethyl sufoxide **11 TS**, and methyl vinyl sulfoxide **18 TS**.

Once the active space is selected, the CASSCF calculation allows a full CI within the active space and re-optimizes the orbitals in a subsequent step. The natural orbital occupation numbers (NOONs), which may resonably assume any value between 0 and 2, are printed out for each orbital of the active space. If the TS contained diradical character, orbitals should be present that have NOONs of approximately 1. For example, ethylene, which most of us think as being closed-shell, has NOONs that are not exactly 2 and 0. The actual NOONs for ethylene at CASSCF[4,4]/6-31G(d,p) are 1.982 (C-C $\sigma$), 1.920 (C-C $\pi$), 0.079 (C-C $\pi^*$), and 0.018 (C-C $\sigma^*$). In all of the transition states studied, the NOONs were either close to zero or close to two, indicating closed shell systems. Table 9 presents above the exact NOONs for all of the TS.

**IRC Description.**[96] IRC calculations have been completed on sulfoxides **8**, **17**, and **18**, each forming a different type of TS. All of the IRC calculations were run at the MP2/6-31G(d,) level unless otherwise noted. The IRC graphs are presented in Appendix 7, Figures 1 - 9. The intrinsic reaction coordinate is defined as the minimum energy path connecting the reactants to products via the transition states. Once the TS is found, the IRC is computed in halves by going forward and backward from the saddle point, down the steepest decent path in mass weighted Cartesian coordinates. The path points of the IRC are in amu$^{1/2}$•bohr. The method used for determining the IRC was the Gonzalez-Schlegel 2$^{nd}$ order method (GS2). The GS2 method is very robust for large step sizes and finds the next point of the IRC via constrained optimization on the surface of a hypersphere, centered at 1/2 the step size along a gradient vector leading from the previous IRC point. A circle tangent to two gradient vectors connects successive IRC points.

The IRC for ethyl methyl sulfoxide **8** shows the C-S bond breaking slightly before the proton is transferred in the transition state (Figure 22). The hydrogen being transferred is nearly halfway, indicating equal C-H bond breakage and H-O bond formation. The transition state resembles neither the starting sulfoxide nor the product. Therefore, since the C-S bond is broken slightly before the hydrogen is transferred, the elimination reaction is a slightly asynchronous concerted process.

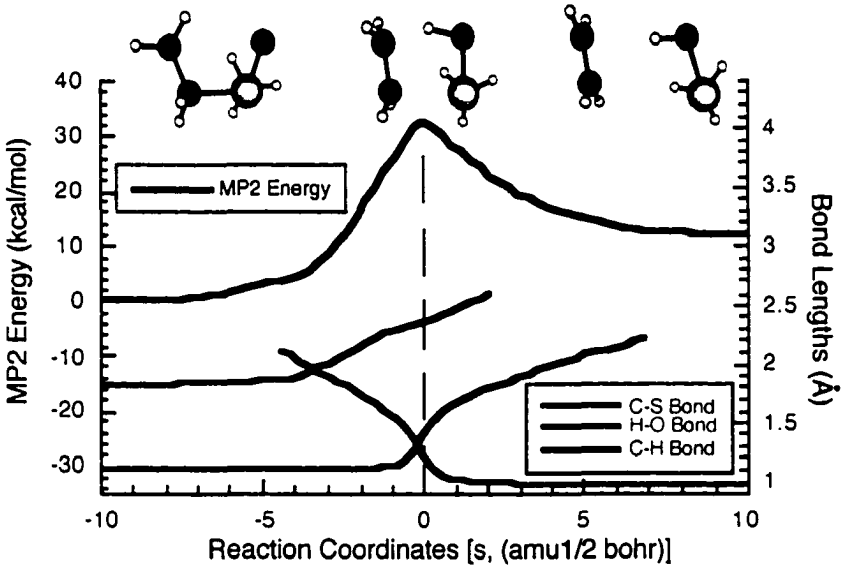


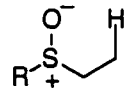

**Figure 22.** IRC for ethyl methyl sulfoxide **8** at the MP2/6-31G(d,p) level.

In Appendix 7, Figure 2, the IRC for 2-butenyl methyl sulfoxide **17** depicts a later transition state **17 TS** as the it resembles the products more than the reactant. The C-S bond is lengthened before the hydrogen is transferred. The proton transfer in the 7-membered TS is much more asynchronous than with ordinary 5-membered TS.

Figure 3 in Appendix 7, presents the IRC for methyl vinyl sulfoxide **18**. The IRC is similar to the IRC for ethyl methyl sulfoxide **8** with the exception that the C-H bond is lengthened earlier and therefore **18 TS** is a later transition state. Again, the IRC depicts an asynchronous process.

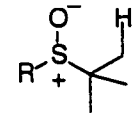
**Energetics**

**Results at MP2/6-311+G(3df,2p)//MP2/6-31G(d,p)** The energetics of the molecules at the MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) level from Groups 1, 2, 3, and 4 are shown in Table 10. Molecules of Group 1 compared the substituents effects at sulfur for methyl, vinyl, phenyl, trifluromethyl groups on the elimination reaction forming their respective sulfenic acid and ethylene. Group 2 sulfoxides investigated the substituents effects at sulfur for hydrogen, fluoro, and amino groups. The sulfoxides in Group 3 evaluated the consequences of having bulky substituents



Group 1

R = $CH_3$ (**8**), $C_2H_3$ (**9**), Ph (**10**), $CF_3$ (**11**)



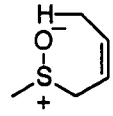
Group 3

R = $CH_3$ (**15**), t-Bu (**16**)

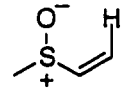
Group 2

R = H (**12**), F (**13**), $NH_2$ (**14**)

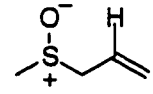
Group 4



**17**



**18**



**19**

**Table 10.** $\Delta H^{\ddagger}$ (kcal/mol) and $\Delta H_{rxn}$ (kcal/mol) for Groups 1-4 at MP2/6-311+G(3df,2p)[a]

| | $\Delta H^{\ddagger}$ (kcal/mol) | | $\Delta H_{rxn}$ (kcal/mol) | |
|---|---|---|---|---|
| Sulfoxide | Computed[a] | Experiment[e] | Computed[a] | Estimated[c] |
| **8** | 32.3 | 33 | 22.6 | 21 |
| **9** | 30.4 | 30 | 20.6 | |
| **10** | 30.6 | | 15.7 | 22[d] |
| **11** | 30.7 | | 18.0 | |
| **12** | 30.0 | | 20.1 | |
| **13** | 42.7 | | 42.6 | |
| **14** | 35.1 | | 28.9 | |
| **15** | 31.4 | | 22.6 | 21 |
| **16** | 27.4 | 25-30[b] | 16.6 | |
| **17** | 47.8 | | 21.1 | 17 |
| **18** | 40.3 | 42 | 28.7 | 31 |
| **19** | 42.8 | | 29.9 | 29 |

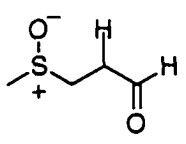
[a]Single point calculations on the optimized MP2/6-31G(d,p) geometry. ZPEs taken from MP2/6-31G(d,p) geometry. [b]See references 51 and 53 for experimental results. [c]See text in Results section for description on estimating $\Delta H_{rxn}$. [d]Estimated using $\Delta H_f^{\circ}$ for PhSOH from reference 97 [e]This study unless otherwise noted, see text.

at sulfur on the elimination reaction. The elimination of methyl t-butyl sulfoxide **15** and di-t-butyl sulfoxide **16** produced isobutylene as a common olefin.

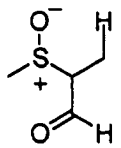
All of Group 4 molecules eliminated to form products that contained two $\pi$ bonds. Sulfoxide **17** eliminated to form 1,3-butadiene through a seven-membered TS and **18** eliminated to form acetylene. The "thermolysis" of allyl methyl sulfoxide **19** produced allene. The latter two reaction proceeded through the normal five-membered TS.

The effect of the acidity of the abstracted proton on elimination reactions with sulfoxides **20** and **21** was studied. Sulfoxides **20** and **21** eliminated to form acrolein and methanesulfenic acid. The effect of having an unsaturated sulfoxide is calculated with **22** and **23**. Both **22** and **23** produced methyl vinyl ketone. All of the sulfoxides in Group 5 tested the effect of producing an $\alpha,\beta$-unsaturated carbonyl. The energetics at MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) are shown in Table 11.

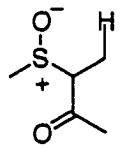
Group 5



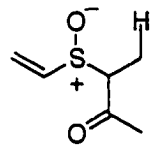
**20**



**21**



**22**



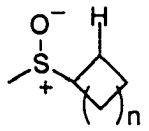
**23**

**Table 11.** $\Delta H^{\ddagger}$ (kcal/mol) and $\Delta H_{rxn}$ (kcal/mol) of Group 5 at MP2/6-311+G(3df,2p)[a]

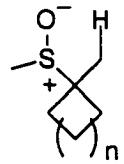
| Sulfoxide | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta H_{rxn}$ (kcal/mol) [Estimated][b] |
|---|---|---|
| **20** | 22.0 | 18.8 [15] |
| **21** | 25.2 | 21.0 [17] |
| **22** | 25.3 | 21.0 [15] |
| **23** | 23.6 | 19.3 |

[a]Single point calculations on the optimized MP2/6-31G(d,p) geometry. ZPEs taken from MP2/6-31G(d,p) geometry. [b]See text in Results section for description on estimating $\Delta H_{rxn}$.

Group 6



n = 0 (**24**), 1 (**25**), 2 (**26**), 3 (**27**)



n = 0 (**28**), 1 (**29**), 2 (**30**), 3 (**31**)

**Table 12.** $\Delta H^{\ddagger}$ (kcal/mol) and $\Delta H_{rxn}$ (kcal/mol) of Group 6 at MP2/6-311+G(3df,2p)[a]

| Sulfoxide | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta H_{rxn}$ (kcal/mol) [Estimated][b] |
|---|---|---|
| **24** | 46.8 | 46.1 [44] |
| **25** | 33.8 | 25.8 [22] |
| **26** | 28.0 | 20.9 [18] |
| **27** | 33.4 | 21.2 [20] |
| **28** | 39.6 | 35.5 [35] |
| **29** | 33.5 | 27.1 [23] |
| **30** | 31.2 | 23.4 [21] |
| **31** | 31.8 | 24.6 [23] |

[a]Single point calculations on the optimized 6-31G(d,p) geometry. ZPE's taken from MP2/6-31G(d,p) geometry. [b]See text in Results section for description on estimating $\Delta H_{rxn}$.

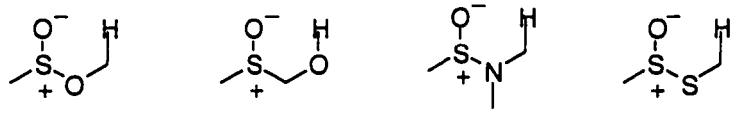
The energetics for the elimination of methanesulfenic acid to produce an olefin in a ring system is shown in Table 12. Group 6 is divided into the types of olefins formed from elimination, sulfoxides **24** – **27** eliminated to form an endo olefin, whereas sulfoxides **28** – **31** reacted to form an exo olefin.

The sulfinyl derivatives in Group 7 will eliminate to form the heteroatom analogs to olefins and methanesulfenic acid. The $\Delta H^{\ddagger}$ and $\Delta H_{rxn}$ are shown in Table 13. Sulfinate ester **32** and α-hydroxy sulfoxide **33** are isomers that both eliminated to form formaldehyde. Comparsion of **32** and **33** provided insight into the effect of acidity of the proton that is transferred during the elimination. Sulfinamide **34** produced methylimine and thiosulfinate ester **35** afforded thioformaldehyde. It should be noticed that $\Delta H_{rxn}$ is higher in energy that $\Delta H^{\ddagger}$ for **33** and **35**. It was insured that the transition state was at a maximum on the potential (an imaginary frequency from the second

derivative). Intrinsic reaction coordinates (IRC) were computed for **32 – 35**. The IRC calculations showed indeed that the TS was a maximum in all of the reactions (Appendix 7 for IRC graphs).

The IRC path at MP2/6-31G(d,p) level for **33** was found to produce a hydrogen-bonded structure (**33 H-bond**) (Figure 23) that was lower in energy the free products (methanesulfenic acid and formaldehyde). This bound structure was then optimized at the MP2/6-311+G(3df,2p), along with the TS, and **33b** (**33a**) to gain a more accurate potential energy surface. Sulfinyl derivatives **33a** and **33b** are conformers. It was found that the $\Delta H^{\ddagger}$ for **33b** (**33a**) increased to 11.4 kcal/mol (6.2 kcal/mol) and that the $\Delta H_{rxn}$ was reduced to 7.9 kcal/mol (2.6 kcal/mol) after the starting material and TS were similarly optimized. The hydrogen-bonded structure for both **33a** and **33b** was shown to be downhill in energy from the TS, 3.6 kcal/mol and 3.5 kcal/mol, respectively. An IRC was run for the **33** at MP2/6-311+G(3df,2p) level and it confirmed the energetics found from the large basis set optimization (Appendix 7). The hydrogen-oxygen bond in **33 H-bond** is calculated to be worth 5.8 kcal/mol at the MP2/6-311+G(3df,2p) level (Figure 23).

Group 7



**32** **33** **34** **35**

**Table 13**. $\Delta H^{\ddagger}$ (kcal/mol) and $\Delta H_{rxn}$ (kcal/mol) at MP2/6-311+G(3df,2p) of Group 7.[a]

| Sulfinyl Derivative | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta H_{rxn}$ (kcal/mol) |
|---|---|---|
| **32a** | 31.5 | 11.3 |
| **32b** | 32.7 | 12.6 |
| **33a** | 5.3 | 8.2 |
| **33b** | 10.3 | 12.4 |
| **34** | 33.2 | 17.2 |
| **35a** | 22.0 | 27.4 |
| **35b** | 21.3 | 26.4 |

[a]Single point calculations on the optimized MP2/6-31G(d,p) geometry. ZPE's taken from MP2/6-31G(d,p) geometry. **a** and **b** are conformers.

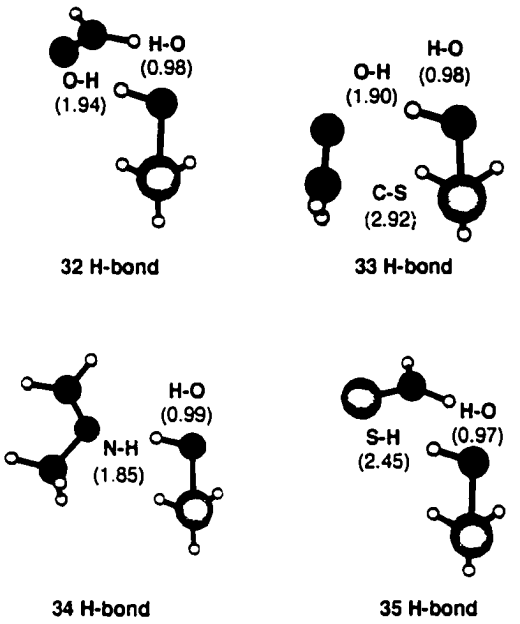



**Figure 23**. Geometries showing hydrogen bonded complexes at the MP2/6-31G(d,p) level. Bond distances in Å.

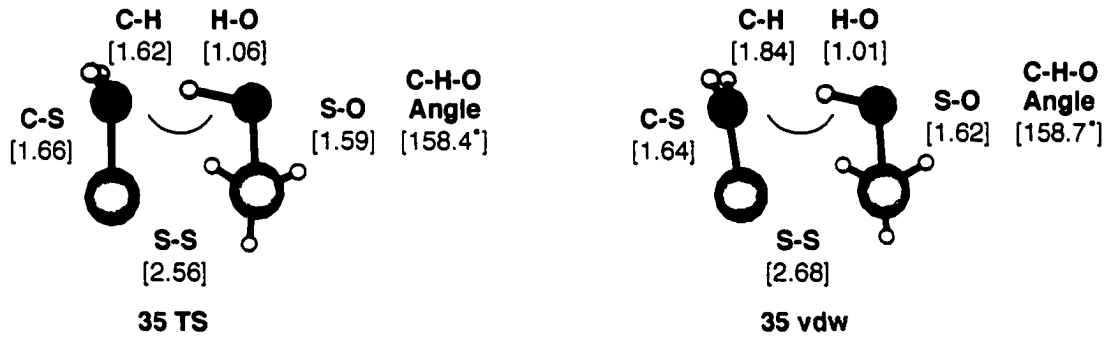



**Figure 24**. Comparison the geometries of methyl thiomethanesulfinate's TS and Van der Waals complex at the MP2/6-311+G(3df,2p) level. **35 vdw** is 0.1 kcal/mol more stable **than 35 TS**. Bond distances are in Å and angles in degrees.

Similar analysis was completed on **35**. The IRC (MP2/6-31G(d,p)) produced a Van der Waals bound product (**35 vdw**) associating thioformaldehyde and methanesulfinic acid (Figure 24). When **35 vdw** was optimized at the MP2/6-31G(d,p) level and the hessian was analyzed, it was found to contain a small imaginary frequency. It was found by decreasing the optimization tolerance and re-optimizing that **35 vdw** disassociated to form a hydrogen-sulfur bound structure (**35 H-bond**)

(Figure 23). However at the MP2/6-311+G(3df,2p) level, **35 vdw** was found to be a minimum on the potential energy surface, 4.6 kcal/mol more stable than free products. Although, when ZPE is added the maximum disappears. At MP2/6-311+G(3df,2p)// MP2/6-31G(d,p), **35 H-bond** was found to have an H-S bond worth 4.5 kcal/mol. The reaction energetics are shown in Table 14.

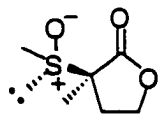
**Table 14.** Energetics[a] of **35a** with TS, Free products, **35** vdw, **35** H-bond.

| Level | $\Delta H^{\ddagger}$ | | $\Delta H_{rxn}$[b] | | | | | |
|---|---|---|---|---|---|---|---|---|
| | No ZPE | ZPE | Free[c] No ZPE | Free w/ZPE | **35 vdw** No ZPE | **35 vdw** w/ZPE | **35 H-bond** No ZPE | **35 H-bond** w/ZPE |
| MP2/6-31G(d,p) | 17.2 | 13.6 | 13.3 | 10.3 | | | 7.4 | 5.8 |
| MP2/6-311+G(3df,2p)// MP2/6-31G(d,p) | 25.6 | 22.0[d] | 30.4 | 27.4[d] | | | 24.5 | 22.9[d] |
| MP2/6-311+G(3df,2p) | 25.9 | 23.3 | 31.2 | 28.3 | 25.8 | 23.9 | 25.1 | 23.3 |

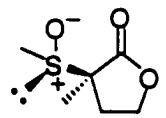
[a]All energies in kcal/mol. [b]**35a** was used as reactant since it was the lowest energy conformer. [c]Free refers to separate calculations for thioformaldehyde and methanesulfenic acid. [d]ZPE energy used from the optimized geometry at the MP2/6-31G(d,p) level.

IRC paths for **32** and **34** lead to hydrogen-bonded complexes that are more stable than the free products. The IRC paths for 32 and 34 are presented in Appendix 7. The hydrogen-bonded structures are shown in Figure 23. The O-H bond in **32 H-bond** is worth 4.3 kcal/mol at the MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) level. The N-H bond in **34 H-bond** is worth 9.2 kcal/mol at the MP2/6-311+G(3df,2p)// MP2/6-31G(d,p) level.

Group 8



**(3R, SR) 36**



**(3R, SS) 36**

The Ei elimination energetics for diastereomers of 3-methanesulfinyl-3-methyl-4,5-dihydro-2-furanone (**36**) were computed. The stereocenter at the 3-methyl substituted center was kept as R in the Prelog nomenclature system. The sulfur stereocenter was varied from R and S. The structures

are named accordingly as **(3R,SS) 36,** referring to the stereoconfiguration R about the carbon center and S about the sulfur center. The transition states are named as **(3R,SR) 36 Exo TS** denoting which starting conformer **(3R,SR) 36** and which product was formed the exo olefin in this example.

Energetics for the elimination reaction of **36** are depicted in Table 15. Three conformers for each diastereomer were found. In Table 15, energetics were computed using the lowest energy conformer (**(3R,SS) 36 Low** and **(3R,SR) 36 Low**) for each diastereomer. Since there are two different beta protons that are accessible for deprotonation, two alkenes can be formed. Deprotonation of the protons on the 3-methyl provided an exo substituted olefin (3-methylene-4,5-dihydro-2-furanone) and deprotonation of the protons on 4-methylene unit lead to an endo substituted olefin (3-methyl-5H-2-furanone). Deprotonation occured through two different TS for each diastereomer for each type of olefin formed (Figure 25). From Figure 25, it is seen that **(3R,SS) Endo TS** is the lowest energy TS with next lowest energy TS being **(3R,SR) Exo TS** lying 2.7 kcal/mol higher in energy. Less than one kcal/mol (0.8 kcal/mol) higher energy **than (3R,SR) Exo TS** is **(3R,SR) Endo TS** and lying much higher in is **(3R,SS) Exo TS**. Figures 26 and 27 are depicting the starting lactone conformers, **(3R,SS) 36** and **(3R,SR) 36**, respectively. The **(3R,SS) 36 Low** was the lowest energy starting conformer with all of the other conformers of both diastereomers being within 6 kcal/mol of each other.

**Table 15**. Energetics[a] at MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) for diastereomers **36**.

| Starting Conformer and TS | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta H_{rxn}$ (kcal/mol) |
|---|---|---|
| **(3R,SR) 36** and **(3R,SR) 36 Endo TS** | 25.0 | 15.6 |
| **(3R,SR) 36** and **(3R,SR) 36 Exo TS** | 24.2 | 23.7 |
| **(3R,SS) 36** and **(3R,SS) 36 Endo TS** | 23.2 | 17.3 |
| **(3R,SS) 36** and **(3R,SS) 36 Exo TS** | 29.8 | 25.3 |

[a]ZPEs are taken from the optimized geometries at MP2/6-31G(d,p).

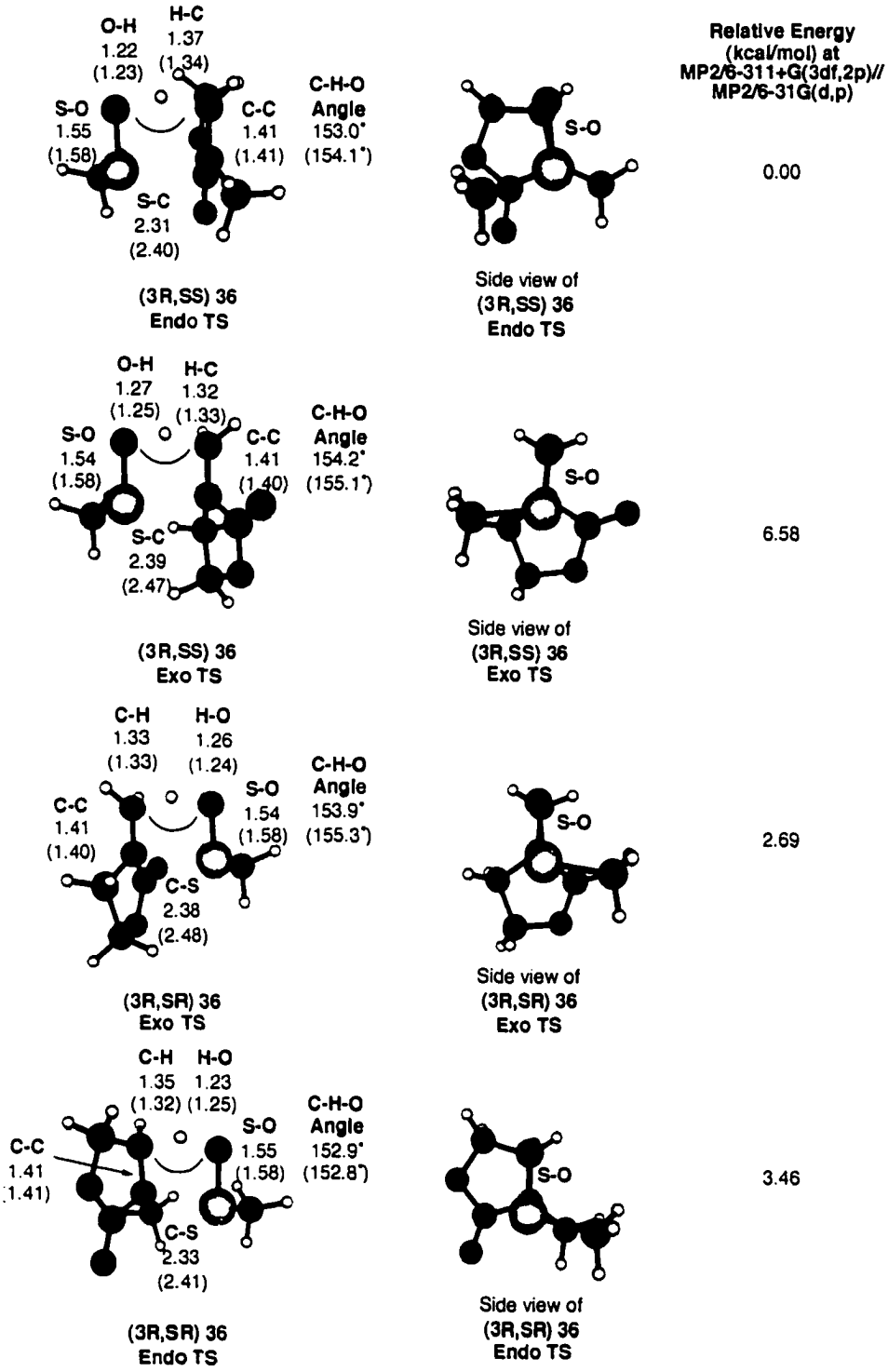
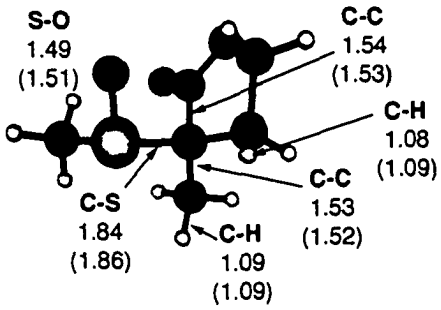
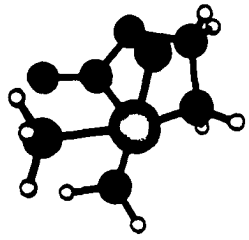



**Figure 25**. Transition States for diastereomers of **36**. Side view is looking down the H-transfer path. The oxygen is obscuring the hydrogen atom being transferred. Bond lengths are in Å.



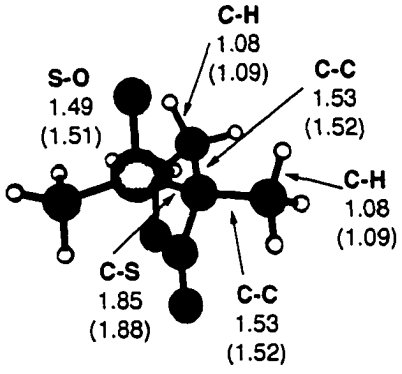

**(3R,SS) 36 Low**



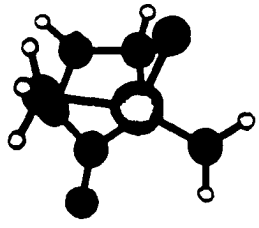
Side view of
**(3R,SS) 36 Low**

**Relative Energy (kcal/mol) at MP2/6-311+G(3df,2p)// MP2/6-31G(d,p)**

0.00

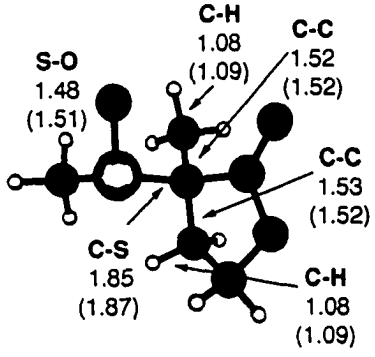



**(3R,SS) 36 Mid**

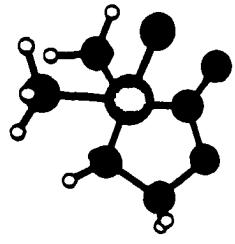


Side view of
**(3R,SS) 36 Mid**

1.51



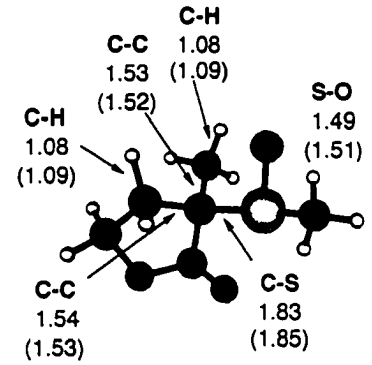

**(3R,SS) 36 High**



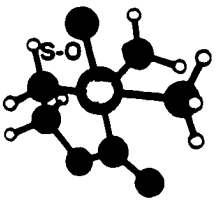
Side view of
**(3R,SS) 36 High**

5.47

**Figure 26. (3R,SS) 36** Starting material conformers. Side view is looking down the S-C bond to show relationship between sulfinyl substitiuent and carbonyl of lactone. Bond lengths are in Å. Energies are relative to **(3R,SS) 36 Low**.



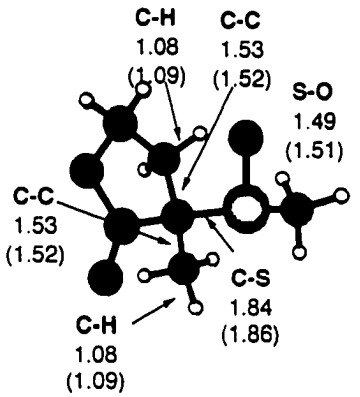

**(3R,SR) 36 Low**



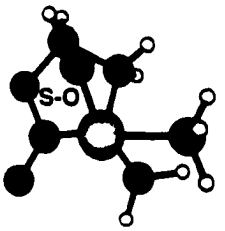

Side view of
**(3R,SR) 36 Low**

**Relative Energies (kcal/mol) at MP2/6-311+G(3df,2p)// MP2/6-31G(d,p) Relative to (3R,SS) 36 Low**

0.00
1.65

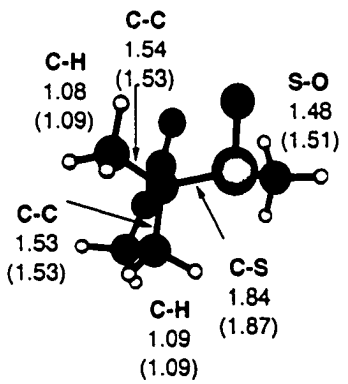



**(3R,SR) 36 Mid**

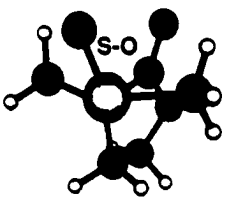



Side view of
**(3R,SR) 36 Mid**

0.87
2.52




**(3R,SR) 36 High**

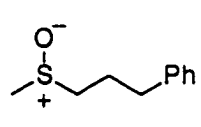



Side view of
**(3R,SR) 36 High**

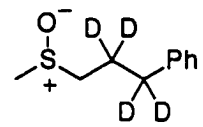
2.77
4.42

**Figure 27. (3R,SR) 36** Starting material conformers. Side view is looking down the S-C bond to show relationship between sulfinyl substitiuent and carbonyl of lactone. Bond lengths are in Å. Energies in black are relative to **(3R,SR) 36 Low** and energies in blue are relative to **(3R,SS) 36 Low** in Figure 26.

**Computed Isotope Effects**. The KIE for the Ei reaction of ethyl methyl sulfoxide **8** vs. its deuterated isotopomers **8a** and **8b** was calculated using the program ISOEFF98,[98,99] which uses vibrational frequencies from the substrate and its respective TS to solve for the KIE using the Bigeleisen equations.[100-102] The KIE was calculated for deuterated isotopomers of **8** at 298 K (4.6 for **8/8a**, 5.0 for **8/8b**, and 1.09 for **8a/8b**) and averaged over the temperature range of the experiments, 503 – 553 K (2.5 for **8/8a**, 2.5 for **8/8b**, and 1.02 for **8a/8b**). From experiment averaged over the temperature range, the $k_H/k_D$ for **1** vs. **1a** was found to be 2.5 ± 0.3. The $k_H/k_D$ for **1** vs. **1b** was found to be 2.8 ± 0.9 averaged over the temperature range. The $k_D/k_D$ for **1a** vs. **1b** was found to be 1.26 ± 0.16 averaged over the temperature range. The calculated KIEs are within experimental error of the experimental KIEs.

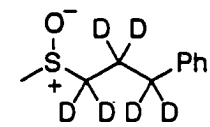


**1**



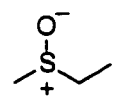
**1a**

$k_1/k_{1a} = 2.5 \pm 0.3$

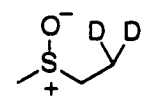


**1b**

$k_1/k_{1b} = 2.8 \pm 0.9$

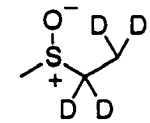


**8**



**8a**

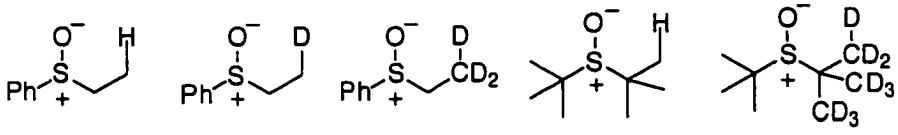
$k_8/k_{8a} = 2.5$



**8b**

$k_8/k_{8b} = 2.5$

Isotope effects were also computed to compared to experimental results (Table 16) of Kwart et al. for alkyl phenyl sulfoxides with ethyl phenyl sulfoxide and its $d_1$-analog (**10/$d_1$-10**).[103] The KIE was calculated for comparison with Yoshimura et al. ethyl phenyl sulfoxide and its $d_3$-analog (**10/$d_3$-10**).[50] Kwart's isotope effects for di-t-butyl sulfoxides were compared to computed KIEs for **16/$d_9$-16**.[53] All of the above experiments where carried out in solution.



**10** **$d_1$-10** **$d_3$-10** **16** **$d_9$-16**

**Table 16**. Comparision of primary kinetic isotope effects with literature measurements

| Temp (K) | $k_H/k_D$ | | Temp (K) | $k_H/k_D$ | | Temp (K) | $k_H/k_D$ | |
|---|---|---|---|---|---|---|---|---|
| | Exp[a] | **10/$d_1$-10** | | Exp[b] | **10/$d_3$-10** | | Exp[c] | **16/$d_9$-16** |
| 298 | — | 4.39 | 298 | — | 5.23 | 298 | — | 5.78 |
| 403 | 3.17 | 3.07 | 353 | 5.15 | 4.14 | 385 | 5.1 | 3.95 |
| 423 | 2.94 | 2.92 | 363 | 4.97 | 3.99 | 395 | — | 3.82 |
| 443 | 2.77 | 2.80 | 373 | 4.77 | 3.85 | 405 | — | 3.70 |
| 463 | 2.63 | 2.68 | | | | 415 | — | 3.59 |
| 483 | 2.49 | 2.58 | | | | 425 | 3.3 | 3.49 |
| 503 | 2.38 | 2.49 | | | | | | |

[a]See Reference 103, [b]See Reference 50, [c]See Reference 53

# Discussion

## Experimental

It is well known in the synthetic literature that a phenyl sulfoxide eliminates more easily than a methyl sulfoxide. This is reflected the 3.1 kcal/mol difference in $\Delta H^{\ddagger}$ for methyl 3-phenylpropyl sulfoxide **1** and vinyl 3-phenylpropyl sulfoxide **2**. The activation enthalpy determined in solution (31.6 kcal/mol)[48] for **1** is in good agreement with our gas-phase value (32.9 kcal/mol). The gas-phase activation data for phenyl 3-phenylpropyl sulfoxide **3** could not be measured, but an upper limit of 30 kcal/mol is reasonable, presuming $\Delta S^{\ddagger}$ is not surprisingly large.[104] The thermolysis experiments have shown the trend of reactivity of the non-reactive sulfoxide substituents to be phenyl > vinyl > methyl. Since it was not possible to measure activaton parameters for sulfoxides **4** and **5** experimentally the discussion of the substituent effects for the trifluouro and amino groups will be deferred to the computational section. Consistent with Yoshimura[50] and Emerson's[46,49] results a negative activation entropy ($\Delta S^{\ddagger}$) effect is observed. The negative $\Delta S^{\ddagger}$ is indicates that an ordered TS is operating.

Formation of acetylene from methyl vinyl sulfoxide **6** shows an activation enthalpy 8.7 kcal/mol higher than formation of allyl benzene from **1**. Thus, the formation of a second pi bond raised the activation barrier a small amount compared to the formation of first pi bond. The vinyl group in formation of acetylene is aided by conformation effects (i.e. the proton being transferred is in the "correct" position to be transfer and does not suffer any entropic effects). This is indicated by the less negative $\Delta S^{\ddagger}$ as seen in Table 4.

Formation of 3-phenylpropanal from 3-phenylpropyl methanesulfinate **7** was found to give a slightly higher activation enthalpy (1.7 kcal/mol) than in **1**. This small increase barrier may be attributable to slightly less basic nature of the sulfinyl substituent in the sulfinic ester versus the sulfoxide. This is consistent with findings of Engberts and Zuidema that sulfoxides are better proton acceptors than sulfinic esters.[65] The very large negative entropy value can partially accounted for by the electron lone-pair lone-pair interaction in rotating into the unfavorable syn-periplanar TS.

## Computational

**Computational Methodology**. Comparison of theoretical models showed that the HF level of theory handled the relative energies of sulfoxides and sulfenic esters poorly. This previously has been shown by Gregory and Jenks.[105] Qualitatively, the correlated models MP2, CCSD(T), and B3LYP provided similar performance, though B3LYP clearly underestimates the activation energies. These trends are consistent with Tronchet's work on amine oxides.[81] Houk has also observed similar trends in [3,3] sigmatropic rearrangements (HF too high, MP2 closest to experiment, and Becke3LYP too low).[106,107] Barone and co-workers have found that Becke3LYP performs poorly with hydrogen transfer reactions, always underestimating the energetics.[108]

**CASSCF Evaluation**. Keeping in mind the findings of Cram and Kingsbury of their proposed radical pathway, a CASSCF method was used to probe transition states **8 – 11 TS**, and **18 TS**. It allowed detection of radical contribution in the transition state, but none was observed for these compounds. The orbital occupation numbers for the transition states were consistent for a closed shell molecule (Table 9). It is thus concluded that the transition state, at least for these sulfoxides, does not contain significant diradical character and is a single reference wavefunction problem.

**Basis Set Effects**. At the MP2/6-31G (d,p) level, when comparing the experimental activation enthalpy of **1** to the computed energy barriers of ethyl methyl sulfoxide **8**, the calculated value is 4.0 kcal/mol lower than the observed experimental value. From the stir-flow experiments, the expected trend in going from a methyl substituent (**1**) to a vinyl substituent (**2**) is a lowering of the activation enthalpy by 3.1 kcal/mol, but when comparing the computation models, sulfoxide **8** to sulfoxide **9**, the trend is not present. The calculated activation enthalpy difference between sulfoxide **8** to vinyl ethyl sulfoxide **9** is only 0.3 kcal/mol with 6-31G(d,p), even at the highest level of theory (CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p). From the computation models at the 6-31G(d,p), the trend in reactivity is trifluoromethyl (**11**) > phenyl (**10**) ~ vinyl (**9**) ~ methyl (**8**).

Comparison of experimental methyl vinyl sulfoxide **6** with computational **18**, identical molecules, the activation enthalpy is still not reproduced with 6-31G(d,p). The $\Delta H^{\ddagger}$ at the MP2/6-31G(d,p) level is 3.7 kcal/mol lower than the observed stirred-flow value.

The basis set study shown in Table 7 clearly outlines that the size of the basis set is very important in predicting activation energy and heat of reaction for the Ei reactions. As in Turecek's DMSO study[83] that compared the sulfoxides versus the sulfenic esters, sulfoxides need to be represented by a very large basis set. Table 7 also provides that the transition state versus sulfoxide ($\Delta H^{\ddagger}$) is less sensitive to basis set size than the products versus sulfoxide ($\Delta H_{rxn}$) which have a true S-O single bond (sulfenic acid). This is shown by the $\Delta H_{rxn}$ changing with smaller increases in the number of basis functions.

The performance of the correlated models and basis set size for $\Delta H_{rxn}$ can be evaluated by comparison to even a smaller model, with sulfoxides and sulfenic acids whose $\Delta H_f^{\circ}$ have been determined experimentally and with very high level calculations. From Benson type empirical calculations,[109] the $\Delta H_f^{\circ}$ were detemined for sulfoxides **8** and **18** to be –42.5 and –10.3 kcal/mol, respectively. From experimental determination at 298 K, the $\Delta H_f^{\circ}$ for ethylene[110], acetylene[110], and methanesulfenic acid[97] are 12.5, 54.5, and –45.4 kcal/mol, respectively. The $\Delta H_{rxn}$ was estimated from Equation 47. The $\Delta H_{rxn}$ for sulfoxides **8** and **18** are 9.6 and 19.4 kcal/mol, respectively. Comparison of the estimated experimental $\Delta H_{rxn}$ with the computed $\Delta H_{rxn}$ values of 21 and 31 kcal/mol for sulfoxides **8** and **18**, respectively, at MP2/6-311+G(3df,2p)//MP2/6-31G(d,p), show the values are in poor agreement.

$$\Delta H_{rxn} = [(\Delta H_f^\circ \text{ sulfenic acid} + \Delta H_f^\circ \text{ alkene/yne}) - (\Delta H_f^\circ \text{ sulfoxide})] \qquad (47)$$

In questioning the experimental value of $\Delta H_f^\circ$ for methanesulfenic acid, a G2 value was used as computed by Gregory in our group.[105] The G2 method has been shown to reproduce the heats of formation for many molecules of similar size within ± 2 kcal/mol.[111] In the worst case, sulfur dioxide's $\Delta H_f^\circ$ deviates by 5 kcal/mol from experiment, thus providing confidence that computed G2 $\Delta H_f^\circ$ will have less than 5 kcal/mol error for methanesulfenic acid. The G2 computed $\Delta H_f^\circ$ value is –33.5 kcal/mol at 298 K for methanesulfenic acid, whereas the experimental $\Delta H_f^\circ$ value is –45.4 kcal/mol.[97] Finding a large difference between G2 value and experiment, made us reevaluate our G2 number. The G2 computed $\Delta H_f^\circ$ value was evaluated cautiously and found to be the same as determined from isodesmic reactions (-33.5 kcal/mol) and from atomization reactions (-33.6 kcal/mol).

When the G2 value for methanesulfenic acid is used in lieu of the experimentally determined $\Delta H_f^\circ$ in equation 47, the large basis set values now are in agreement with the empirical estimates (Table 10). The estimated experimental $\Delta H_{rxn}$ is 21 kcal/mol for sulfoxide **8** and is 31 kcal/mol for sulfoxide **18**. The G2 value is now believed to be correct, or at least closer than the reported experimental value. Providing added confidence in the G2 value for methanesulfenic acid, there are several more examples of $\Delta H_{rxn}$ values in Tables 10, 11, and 12. These values generally give estimated $\Delta H_{rxn}$ within 4 kcal/mol of the calculated $\Delta H_{rxn}$ for the elimination reactions using the G2 value for methanesulfenic acid and Benson values sulfoxides. Sulfoxide **10** was calculated using an experimental $\Delta H_f^\circ$ value for benzenesulfenic acid[97] and ethylene[110], and Benson value for **10**.[109] It gave an estimated $\Delta H_{rxn}$ with somewhat of a larger deviation from the calculated value, but at least it is still in the ballpark.

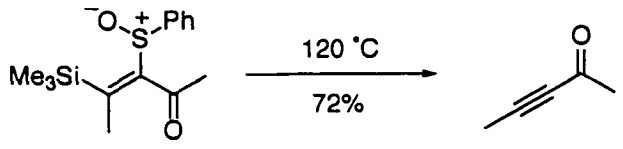
Now with confidence in the level of theory and basis set size, comparision of the calculations can be made to establish the trends of the effect of eliminating other types of molecules that are not compatible with gas-phase experiments. This will tie together the past literature on Ei reaction of sulfoxides.

**Non-Reactive Substituent Effects**. As seen with from the Hammett correlation studies by Yoshimura et al.[50] and Emerson et al.[46], all of the electron withdrawing groups have been shown to

have a stabilizing effect of the transition state. We should expect the same trend when electron withdrawing groups are attached directly at carbon. The trends at the MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) level from Table 10 for Groups 1 and 2 are phenyl (**10**) ~ vinyl (**9**) ~ trifluoromethyl (**11**) ~ hydrogen (**12**) > methyl (**8**) > amino (**14**) >> fluoro (**13**). Most remarkable is the subtlety of change in activation enthalpy from substituent to substituent, i.e. phenyl through amino. Overall the energy differences between products ($\Delta H_{rxn}$) and TS ($\Delta H^{\ddagger}$) (i.e. $\Delta H^{\ddagger}_{backrxn}$) are unremarkable, all are consistently about 10 kcal/mol for sulfoxides **8** – **14**, save **13**. Fluoro substituted sulfoxide **13** has a barrier some 10 kcal/mol higher in energy than **8**. This effect can be accounted for by looking at $\Delta H_{rxn}$ for **13**. It provides that the products of the elimination are of high energy (i.e. FSOH). This might imply that the geometry of **13 TS** is late but actually it is very similar to that of **8 TS** and does not appear product-like (Appendix 2, Figure 9). Overall, the energy differences $\Delta H^{\ddagger}$ are unremarkable only slight increases in energy are observed in going from vinyl **9** to methyl **8** to amino **14** (Table 10).

**Steric Effects**. Group 3 sulfoxides were calculated and match well the experimental barriers of Shelton[51] and Kwart.[53] A rate acceleration was observed from steric crowding for di-t-butlyl sulfoxide **16** and the calculated barrier predicts a 4 kcal/mol lower barrier than that for methyl t-butyl sulfoxide **15**. In fact, steric crowding about **16** forces the t-butyl groups to be twisted and $C_1$ not $C_s$ in symmetry. Comparison of **15** with **8** shows only a slight reduction in $\Delta H^{\ddagger}$ (1 kcal/mol), but shows that great rate acceleration comes from the second t-butyl group. Di-t-butyl sulfoxide **16** has a C-S-C bond angle of 112° (at MP2/6-31G(d,p) geometry) some 15° greater than the bond angle in DMSO (96°).[93] The second t-butyl group promotes destabilization of the ground state which accounts for the lower barrier. Comparison of $\Delta H^{\ddagger}$ - $\Delta H_{rxn}$ for **15** and **16** give similar barriers for the reverse reaction, again about 10 kcal/mol.

**Mutiple Bond Formation**. Sulfoxides in Group 4 all formed an extra $\pi$ bond upon thermolysis. Experimental and computational agreement was found with methyl vinyl sulfoxide (**6** = **18**). This is the first example of Ei reaction producing an alkyne and a sulfenic acid from a true sulfoxide, although Flemming and collegues have produced alkynes in the elimination reaction (equation 48).[57]




(48)

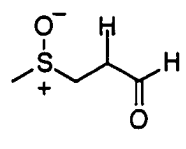
Sulfoxide **17** was found to produce butadiene through a seven-membered TS with a barrier of 47.9 kcal/mol at the MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) level. The much higher activation barrier can be attributed to the ring strain in forming the seven-membered TS (about 25 kcal). The flexibility of the seven-membered TS allowed the hydrogen transfer angle (C-H-O angle) to flatten out slightly to 162°. This system has the largest $\Delta H^{\ddagger}$ - $\Delta H_{rxn}$ (27 kcal/mol) of all of the compounds studied, further indication of ring strain in formation of the transition state.

Computationally, the $\Delta H^{\ddagger}$ for formation of allene with allyl methyl sulfoxide **19** was found to be 43 kcal/mol. This value was only 3 kcal/mol higher than the barrier for the formation of acetylene with methyl vinyl sulfoxide **18**. This is accounted for in the reverse barriers. Both reverse barriers for **18** and **19** show the 3 kcal/mol trend, $\Delta H^{\ddagger}$ - $\Delta H_{rxn}$, for the addition of acetylene and allene to methanesulfenic acid are 11 and 13 kcal/mol, respectively. It should be noted that the experiment could not be performed on this compound due to its ability to undergo the [2,3] sigmatropic rearrangement with a much lower barrier (about 23 kcal/mole for similar molecules).[112]

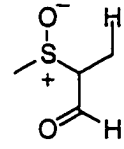
**Acidity Effects**. To study the effect of acidity on the β-hydrogen, sulfoxide **20**, containing an acidic β-hydrogen, was compared to its isomer sulfoxide **21** without an acidic β-hydrogen. Sulfoxide **20** eliminated with an activation enthalpy 3 kcal/mol lower than **21**. Since these are isomers the $\Delta H_{rxn}$ should be the same if there are not modest confromational or isomeric energy effects in the starting materials. The $\Delta H_{rxn}$ for **20** is 3 kcal/mol lower in energy than the $\Delta H_{rxn}$ for **21**. This indicates that starting geometry is 3 kcal/mol less stable for **20** than for **21**. Therefore, the barriers are very similar and the 3 kcal/mol is probably not big enough to worry about. Nonetheless, the lowering of the activation barrier is consistent with slight rate acceleration observed by Crich[56] and Shelton[51] with eliminations of sulfoxides that contained acidic β-hydrogens.

The TS geometry changes slightly for the elimination of sulfoxides with acidic β-hydrogens. In general, the hydrogen transfer angle (C-H-O) is about 154° for transition states of ordinary eliminations (i.e. ethyl methyl sulfoxide **8**). However, the transfer angle in **20 TS** was more acute (149°). In

addition, **20 TS** was more product like than **21 TS**, i.e. the hydrogen was transferred earlier and C-S bond was broken less (0.25 Å) than in **21 TS** (Appendix 2, Figures 14 and 15).



**20**



**21**

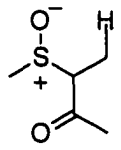
In another test for acidity, the energetics for the elimination reaction for the hypothetical molecule in equation 49 was evaulated. This reaction allowed access to the acidity effect inductively, without conjugative inteferrence. At the MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) level, the activation enthalpy ($\Delta H^{\ddagger}$ = 19.3 kcal/mol) and heat of reaction ($\Delta H_{rxn}$ = 16.9 kcal/mol) were calculated. These $\Delta H^{\ddagger}$ values are most notably lower than the in normal alkyl sulfoxide (~10 kcal/mol) and even 3.0 kcal/mol lower than in **20**. The TS was very product like. The hydrogen transfer occurred earlier, as with **20**. In addition, the O-H bond is almost formed in the TS and the transfer angle (147°) of C-H-O is the most acutely bent of all the sulfoxides studied.

(49)

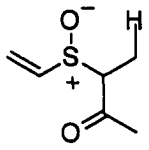
$\Delta H^{\ddagger}$ = 19.3 kcal/mol

$\Delta H_{rxn}$ = 16.9 kcal/mol

Group 5 compounds also gave access into the energetics in forming α,β-unstaturated carbonyls. All of the sulfoxides provided a much lower activation barrier (25 kcal/mol) than the corresponding alkyl sulfoxides (30 kcal/mol). This lower activation barrier is due to the carbonyl stabilization of the transition state as pointed out by Shelton[51] and shown in Figure 7. The Group 5 reverse barrier ($\Delta H^{\ddagger}$ - $\Delta H_{rxn}$) for the addition of acrolein or methyl vinyl ketone to methanesulfenic acid was very small only 2 – 4 kcal/mol. This barrier is much smaller than the $\Delta H^{\ddagger}$ - $\Delta H_{rxn}$ for Group 1 sulfoxides. These data indicate that the reverse reaction of sulfenic acid addition to an unsaturated olefin should be facile with such a small barrier.



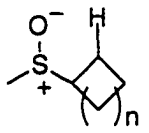
**22**



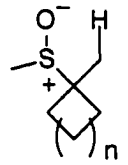
**23**

The computation of the barriers for sulfoxides **22** versus **23** allowed a rationale for ease of elimination phenyl sulfoxides versus alkyl sulfoxides. In sulfoxide **23** the vinyl group is acting as the phenyl group equivalent and indeed there is a slight lowering in activation enthalpy with vinyl substituent is observed (3 kcal/mol). The small substituent (methyl versus vinyl) effect measured for **1** and **2** experimentally is again shown. This is consistant with the findings from Trost's group.[3]

Group 6



n = 0 (**24**), 1 (**25**), 2 (**26**), 3 (**27**)



n = 0 (**28**), 1 (**29**), 2 (**30**), 3 (**31**)

**Ring Effects**. The calculated activation enthalpies for sulfoxides **24** - **27** produced barrier heights consistent with the effect of ring size on the rate of elimination for the formation of endo alkenes observed by Kice and Campbell.[55] The barriers are in the order of ring size cyclopentyl **26** < cyclohexyl **27** ~ cyclobutyl **25** << cyclopropyl **24**. As seen in Appendix 2, Figure 18, the cyclopropyl elimination forming a very high energy product (cyclopropene) produced a late transition state **24 TS**. As predicted in the amine oxide eliminations[42] and by Kice[55], cyclopentyl methyl sulfoxide **26** is in the correct conformation to undergo elimination in **26-TS** (Appendix 2, Figure 20). However, sulfoxide **27** has to undergo ring flattening to a psuedo axial conformation (**27 TS**, Appendix 2, Figure 21) in order for the elimination to occur. This ring flattening is also observed in cyclobutyl methyl sulfoxide **25 TS**. All of these transition states are fairly similar in that the C-S bond is broken more and then the hydrogen is transferred somewhat symmetrical. With the exception of sulfoxide **24**, the reverse reacton barriers $\Delta H^{\ddagger}$ - $\Delta H_{rxn}$ are 8, 8, and 13 kcal/mol for **25**, **26**, and **27**, respectively. These compare closely with the reverse barriers of Group 1.

The barriers for the formation of the exo alkenes from sulfoxides **28** to **31**was provided. The barriers are in the order of rings size cyclopentyl **30** ~ cyclohexyl **31** > cyclobutyl **29** > cyclopentyl **28**. Again the cyclopropyl sulfoxide **28** contained a late TS, with formation of the O-H bond almost complete (Appendix 2, Figure 22). The other sulfoxides all containing similar transition states with C-S bond being elongated and the hydrogen transfer is taking place almost symmetrical. The $\Delta H^{\ddagger}$ - $\Delta H_{rxn}$ values were 4, 6, 8, 7 kcal/mol for **28**, **29**, **30**, and **31** respectively.

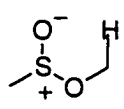
One alicyclic ring opening was calculated for the episulfoxide in equation 50. Foote and Greer, have experimentally determined activation enthalpy to be 18 kcal/mol though this value is not yet published. The calculated value of 20.0 kcal/mol at the MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) level is in good agreement with the experiment. The $\Delta H_{rxn}$ is computed to be only slightly endothermic (0.5 kcal/mol) is also consistent with Baldwin's data (i.e. ring opening occured at 35°C).[59]


(50)

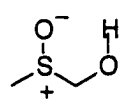
**Sulfinyl Derivatives**. The calculated activation enthalpy ($\Delta H^{\ddagger}$ = 32.7 kcal/mol) at the MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) level for the sulfenate ester **32** elimination, forming formaldehyde, was in close agreement with the stirred-flow determined value with 3-phenylpropyl methanesulfinate ($\Delta H^{\ddagger}$ = 34.6 kcal/mol). To the best of the author's knowlegde, this is the first example providing an aldehyde from a sulfinic ester.

The α-hydroxy analog **33** was calculated to have a much lower barrier ($\Delta H^{\ddagger}$ = 10.3 kcal/mol) for formation of formaldehyde than with the ester **32**. This is in agreement with a result from Clennan's group.[113] His group has proprosed that α-hydroxy sulfoxides are transient intermediates that are formed in the reaction of singlet oxygen with alkyl sulfides. The transient α-hydroxy sulfoxides assumed to decompose to sulfenic acids and carbonyl compounds very rapidly.

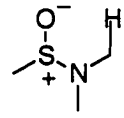
Group 7



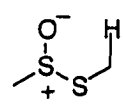
**32**



**33**



**34**



**35**

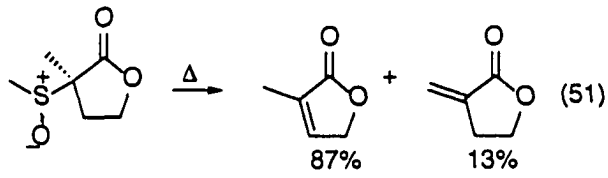
Giving that the products and starting sulfinyl derivatives **32** and **33** are of approximately equal energy (α-hydroxy 1.1 kcal/mol more stable), the difference in the barrier comes from a huge stabilization energy (24.6 kcal/mol) of the transition state in **33**. The acidity of the proton transferred and increased basicity in the sulfinyl group's oxygen in **33** can account for the stabilization energy. The calculated transition state **33 TS** has the proton being transferred before breaking of the C-S bond. As is the case with all of the acidic hydrogen transfers, the early hydrogen transfer forces the C-H-O angle (149.5°) to be more bent than with the ordinary sulfoxides (154°). The $\Delta H^{\ddagger}$ - $\Delta H_{rxn}$ value is remarkable for **32**, the reverse reaction has a much higher barrier due to stabilization of the product, i.e. the carbonyl formed in **32** is more stable than ethylene as formed in methyl ethyl sulfoxide **8**.

The elimination to form methylimine was fairly normal for N,N-dimethy methanesulfinamide **34**. The reaction energetics were $\Delta H^{\ddagger}$ of 33.2 kcal/mol and $\Delta H_{rxn}$ of 17.2 kcal/mol. The $\Delta H^{\ddagger}$ - $\Delta H_{rxn}$ value is somewhat higher to due to the product stabilization in formation of methylimine. The IRC path led to finding a hydrogen-bonded structure that was more stable than free products by 9 kcal/mol. The practical issue for synthetic use lies in the stability of imines produced, but the barrier should not limit this reaction from being utilized.

Thiosulfinate **35** eliminated to produce thioformaldehyde with a barrier of 22 kcal/mol. Most notable of this reaction is the flatness of the reaction potential (Appendix 7, Figure 9). Although free products are higher in energy than the transition state, there are two calculated weakly bound states that, one hydrogen-bonded and the other through a Van der Waals interaction. The transition state contains the least bent hydrogen transfer angle of any of the five-membered planar transition state. This is easily accounted for by the length of the S-S bond. The fact that this barrier is so low is due in part to the weak S-S bond and the increase acidity of the β-hydrogen. The fact that Block and co-workers have observed many products arising from this simple elimination[67] can be accounted for with the high energy product.

Finally, Group 7 molecules contain a widely diverse set of reaction barriers. All products can form hydrogen-bonded products that are lower in energy than the free products. The reaction energetics produced the order barriers to be α-hydroxy **33** << thio ester **35** << ester **32** ~ amide **34** with later two giving activation barriers most similar to that of sulfoxide **8**.

**Diastereomer Effects**. The computational elimination barriers for diastereomers of **36** are in qualitative agreement with experiments of Trost and co-workers.[7,8] The exo olefin formation is favored in diastereomer **(3R, SR) 36** by only 1.2 kcal/mol over formation of the endo olefin, whereas with diastereomer **(3R, SS) 36**, the formation of the endo olefin is preferred by 6.6 kcal/mol over the exo olefin. Since Trost's results did not report the ratio of non-separatated diastereomers that was pyrolyzed in equation 51, the calculations predict that both diastereomers could form the endo olefin, whereas only with **(3R, SR) 36** could feasibly form the exo olefin. These calculations show dipoles are significant not only starting sulfoxides but also in transition states, as the dipoles can stabilize preference of one diastereomer over another. From these results a much more interesting experiment would be to prepare and separate both diastereomers. Then carry out the pyrolysis on each separate olefin and observe the exo/endo olefin distributions.



(51)

**Isotope Effects**. Good correlation is found between experimental values and computed values for sulfoxides **1**, **1a**, **1b**, and **8**, **8a**, and **8b**, respectively. The observed isotope effect ($k_H/k_D$= 2.5 – 2.8) is adding data consistent with previous literature,[50,53,103] i.e. the hydrogen is transferred in a bent transition state. Our calculations with **10** and **$d_1$-10** compared to Kwart's experimental KIE values[103] are in excellent agreement, lending to confidence in the ISOEFF98 program.[99] The calculated KIE for **10** and **$d_3$-10** are again in ballpark agreement as were **16** and **$d_3$-16** (Table 5). The deviations from the calculated KIE from being closer to the experimental values could lie in solvent effects that were not accounted for in the gas phase computations.

# Conclusions

The stirred-flow experiments have allowed access to activation parameters for a variety of sulfoxides and sulfinyl derivatives. Activation enthalpies were found for the formation of alkynes from unsaturated sulfoxides and aldehydes from sulfinic esters. The elimination reaction with formation of an alkyne occurred with a 10 kcal/mol higher barrier and the formation of aldehydes from sulfinic esters occurred with only a slightly higher barrier as compared to the formation of alkenes.

Calculations of the activation energies for the model compounds compare closely with experiment. Becke3LYP level has been shown to perform poorly in describing the Ei reactions (always predicting barriers that are too low). MP2 and CCSD(T) levels performed similarly; the major effect was the basis set. It was imperative to use a very large basis set to describe the sulfoxides correctly. The 6-311+G(3df,2p) basis set was used in achieving agreement between theory and experiment. The CASSCF level calculations have shown no radical character in the transition state for the sulfoxides studied.

Experiment and theory are in agreement with the classical concerted elimination mechanism. In most instances, the C-S bond was broken before the hydrogen transfer in the transition state, unless the hydrogen being transferred was acidic. From calculations, barriers for elimination were lower for sulfoxides and derivatives containing acidic protons, where steric effects existed, and in carbonyl systems. Ei barriers were much higher for sulfoxides that formed high energy products, larger membered transition states, and additional pi bonds. For the diastereomers in the lactone system, it was shown that not only the conformations (energy) of the starting sulfoxide was important but also the energy of the transition state in determining which olefin was formed.

# Experimental Section

## Instrument

The stirred-flow reactor has a temperature-controlled furnace and is modeled very closely after the one that has been previously described.[84] It uses He as a carrier gas to bring the sample into a quartz reactor (clean, and silylated) whose volume controls the residence time, which is a few seconds. Samples were injected as concentrated solutions in acetonitrile. After the furnace section, the gases are sent to a GC that operates at lower temperatures, where starting materials and products

are separated and quantified. Rate constants are extracted from each run, and multiple injections were made at each temperature. All sulfoxides thermalized were greater than 99% purity, as determined by the observation of a single peak by GC without thermolysis.

## Compound preparation

**General.** Unless otherwise noted, starting materials were obtained from Aldrich and used as received. Characterization was carried out on a Bruker Avance DXR NMR operating at 400 MHz for proton and 100 MHz for carbon. The $^{13}C$ signals for $CD_2$ carbons were generally not observed due to the low signal-to-noise and high multiplicity. MS were obtained on a Finnigan TSQ 700 operating in EI mode. IR spectra were obtained on a Mattson Gallaxy Series FTIR 3000. Dry THF was freshly distilled from benzophenone ketyl. Sulfoxides **2** and **3** were prepared by Guo in our lab.[104] For the AB quartet in **1a** $\Delta\nu/J$ was calculated using: $\Delta\nu/J = (4C^2 - J^2)^{1/2}/J$; C = separation from first peak to third peak and J = separation from first to second peak in the quartet.

**General procedure for preparation of sulfoxide from sulfide.** For a good general reference for the synthesis of sulfides to sulfoxides see Mata's review.[114] To an ice cooled solution of 2-3 mmol of the sulfide in methylene chloride (15 mL) was added 1.0 equivalents of m-chloroperbenzoic acid dissolved in 25 mL methylene chloride dropwise by means of a dropping funnel. After two hours, the mixture was poured in to aqueous NaOH (5%, 50 mL) and the layers were separated. The organic layer was washed with another portion of aqueous NaOH, then dried with $MgSO_4$ and concentrated in vacuo. Further purification was carried out as noted. Isolated yield in the range of 60 to 80%.

**Methyl 3-phenylpropyl sulfide.** To a suspension of NaH (0.94 g, 0.039 mol) in THF (20 ml) at 0 °C, under Ar, 3-phenylpropylthiol (2.0 g, 0.013 mol) was added dropwise. The thiol was cautiously added over 10 min due to very rapid $H_2$ evolution. To the stirred solution, methyl iodide (5.53 g, 0.039 mol) in THF (15 ml) was added dropwise and the ice bath was removed. The reaction was monitored by TLC (75% hexane/25% EtOAc) and the mixture was stirred at room temperature for 3 h. The reaction mixture was poured into water (50 ml) and the layers were separated. The aqueous layer was extracted with ether (3 x 25 ml). The organic layers were combined, dried ($MgSO_4$), and concentrated to give the sulfide in greater than 99% yield. This could be oxidized to sulfoxide without

further purification. $^1$H NMR ($CDCl_3$) δ 7.29 – 7.24 (m, 2 H), 7.21 – 7.16 (m, 3 H), 2.70 (t, J = 7.6 Hz, 2 H), 2.49 (t, J = 7.2 Hz, 2 H), 2.08 (s, 3 H) 1.92 (quint, J = 15.2 Hz, 2 H), $^{13}$C NMR ($CDCl_3$) δ 141.7, 128.5, 128.4, 125.9, 34.8, 33.7, 30.7, 15.5.

**Methyl 3-phenylpropyl sulfoxide (1)**. Hydrogen peroxide (30%, 1.36 g, 0.012 mol) was added dropwise to a solution of methyl 3-phenylpropyl sulfide (1.00 g, 0.006 mol) in methanol (25 ml). The reaction mixture was allowed to stir for 42 h. The reaction was monitored by TLC (50% hexane/50% EtOAc). Water (30 ml) was added and the solution was washed with $CH_2Cl_2$ (3 x 25 ml). The organic layer was dried ($MgSO_4$) and concentrated. The yellow oil was put under reduced pressure overnight and the oil became a light yellow solid. The sulfoxide was purified first by flash chromatography (4 $CH_2Cl_2$/1 EtOAc) and then recrystallized at low temperature in ether to afford white cyrstals in 64 % yield. $^1$H NMR ($CDCl_3$) δ 7.33 – 7.27 (m, 2 H), 7.22 – 7.18 (m, 3 H) 2.80 (t, J = 7.5 Hz, 2 H), 2.61 – 2.73 (m, 2 H), 2.54 (s, 3 H), 2.09 – 2.17 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 140.4, 128.6, 128.5, 126.4, 53.8, 38.6, 34.2, 24.2. IR (thin film) 3024, 2922, 2859, 1453, 1044, 747, 700 cm$^{-1}$.

**Ethyl 2,2,3,3-tetradeutero-3-phenylpropionate**. In a 250 mL round bottom flask, ethyl phenylpropiolate (10.0 g, 57.4 mmol) was dissolved in diethyl ether (10 mL) and Pd/C (2.0 g) was added. The mixture was stirred rapidly and $D_2$ was introduced into the chamber as follows: a three-way valve was attached to the deuterium source, the reaction flask, and a calibrated U-shaped tube (1.4 L) filled with mineral oil. The reaction was run until completion as monitored by GC. The mixture was filtered and concentrated to give the product in 86% yield. The product was clean by NMR and used for subsequent steps. $^1$H NMR ($CDCl_3$) δ 7.3 -7.18 (m, 5H), 4.13 (q, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$) δ 173.2, 140.7, 128.7, 126.4, 60.6, 14.4. IR (thin film) 3026, 2981, 2222, 2101, 1732, 1268, 1026, 735, 699 cm$^{-1}$.

**2,2,3,3-tetradeutero-3-phenyl-1-propanol**. To a suspension of lithium aluminum hydride (0.63 g, 16.5 mmol) in dry THF (25 mL) under Ar at O °C, ethyl 2,2,3,3-tetradeutero-3-phenylpropionate (1.0 g, 5.49 mmol) was added. The suspension was allowed to warm to room temperature. After stirring one hour the reaction mixture was heated to reflux for five hours. The reaction was quenched by slow, successive addition of $H_2O$ (0.6 mL), aq. NaOH (0.6 mL), and $H_2O$ (1.8 mL). The solution was filtered then poured into ether (30 mL) and washed with brine (3 x 25 mL). The organic layer was dried ($MgSO_4$) and concentrated to give

2,2,3,3-tetradeutero-3-phenyl-1-propanol in 98% yield. The material was clean by NMR and used in the next step without further purification. $^1$H NMR ($CDCl_3$) δ 7.29-7.16 (m, 5H) 3.65 (s, 2H), 1.64 (s, 1H) $^{13}$C NMR ($CDCl_3$) δ 141.8, 128.5, 128.5, 125.9, 62.2. IR (thin film) 3346, 3024, 2918, 2876, 2206, 2112, 1604, 1043, 699 $cm^{-1}$.

**2,2,3,3-tetradeutero-3-phenylpropyl p-toluenesulfonate.**[115] In a round bottom flask (50 mL), 2,2,3,3-tetradeutero-3-phenyl-1-propanol (0.7 g, 5.0 mmol) was dissolved in chloroform (10 mL) and cooled in an ice bath (0° C). To the solution, pyridine (0.8 g, 10.0 mmol) was added, followed by p-toluenesulfonyl chloride (1.4 g, 7.5 mmol). The reaction was monitored by TLC and completed after stirring 2.5 h. To the mixture, ether (30 mL) and water (15 mL) were added and the layers were separated. The organic layer was washed successively with HCl (2N, 20 mL), $NaHCO_3$ (5%, 20 mL), and water (25 mL). The solution was dried ($MgSO_4$) and concentrated. Flash chromatography (75/25 Hexane/EtOAc ) was use to obtain a clean sample in 80% isolated yield. $^1$H NMR ($CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.22 (t, J = 7.2 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 7.2 Hz, 2H), 4.01 (s, 2H), 2.43 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 144.8, 140.3, 133.1,129.9, 128.5, 128.5, 128.0, 126.2, 69.6, 21.7. IR (thin film) 3060, 2985, 2209, 2118, 1598, 1356, 1177, 919, 663 $cm^{-1}$.

**Methyl 2,2,3,3-tetradeutero-3-phenylpropyl sulfide**. To a solution of sodium thiomethoxide (0.53 g, 7.6 mmol) in dry ethanol (15 mL) under Ar, 2,2,3,3-tetradeutero-3-phenylpropyl p-toluenesulfonate (0.75 g, 2.5 mmol) dissolved in dry THF (20 mL) was added. The mixture was stirred for three hours. The mixture was poured into water (25 mL) and the aqueous layer was extracted with ether (3 x 25 mL). The combined organic layers were washed successively with brine (2 x 25 mL) and water (2 x 25 mL). The mixture was dried ($MgSO_4$) and concentrated to yield methyl 2,2,3,3-tetradeutero-3-phenylpropyl sulfide in 98% yield. $^1$H NMR ($CDCl_3$) δ 7.29-7.24 (m, 2H), 7.20-7.15 (m, 3H), 2.48 (s, 2H), 2.08 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 140.8, 128.5, 128.4, 125.9, 33.4, 15.5. IR (thin film) 3059, 3024, 2914, 2205, 2101, 1603, 909, 733, 700 $cm^{-1}$.

**Methyl 2,2,3,3-tetradeutero-3-phenylpropyl sulfoxide (1a)** was prepared from oxidation of methyl 2,2,3,3-tetradeutero-3-phenylpropyl sulfide (0.08 g, 0.05 mmol) with mCPBA as described above in quantitative yield. It was further purified by recrystallization from ether at low

temperature yielding white crystals (65% yield). $^1$H NMR ($CDCl_3$) δ 7.29-7.26 (m, 2H), 7.21-7.15 (m, 3H), 2.95 ($q_{AB}$, J = 13 Hz, Δν/J = 5.5, 2H), 2.51 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 140.3, 128.8, 128.5, 126.6, 53.7, 38.6. EI-MS (m/e, relative abundance) 186 (27), 120 (100), 93 (48). IR (thin film): 3021, 2953, 2905, 2206, 2106, 2090, 1301, 1133, 1028, 744, 703 $cm^{-1}$.

**2,2,3,3,4,4-hexadeutero-3-phenyl-1-propanol**. It was prepared using the above reduction procedure from the preparation of 2,2,3,3-tetradeutero-3-phenyl-1-propanol. Lithium aluminum deuteride was substituted for lithium aluminum hydride as the reducing agent. It was used as found for next step. $^1$H NMR ($CDCl_3$) δ 7.31-7.27 (m, 2H), 7.21-7.18 (m, 3H), 2.14 (broad s, 1H); $^{13}$C NMR ($CDCl_3$) δ 141.9, 128.5, 128.5, 125.9.

**2,2,3,3,4,4-hexadeutero-3-phenylpropyl p-toluenesulfonate**.[115] In a round bottom flask (50 mL), 2,2,3,3,4,4-hexadeutero-3-phenyl-1-propanol (1.0 g, 7.0 mmol) was dissolved in chloroform (10 mL) and cooled in an ice bath (0° C). To the solution, pyridine (1.1 g, 14.0 mmol) was added, followed by p-toluenesulfonyl chloride (2.01 g, 11.0 mmol). The reaction was monitored by TLC and completed after stirring 2.5 h. To the mixture, ether (30 mL) and water (15 mL) were added and the layers were separated. The organic layer was washed successively with HCl (2N, 20 mL), $NaHCO_3$ (5%, 20 mL), and water (25 mL). The solution was dried ($MgSO_4$) and concentrated. Flash chromatography (90/10 Hexane/EtOAc ) was use to obtain a clean sample in 90% isolated yield. $^1$H NMR ($CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.14 (tm, J = 7.6 Hz, 2H), 7.14 (td, J = 7.2 and 1.6 Hz, 1H), 7.05 (dm, J = 6.8 Hz, 2H), 2.43 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 144.9, 140.4, 133.3, 130.0, 128.5, 128.5, 127.9, 126.2, 21.7

**Methyl 2,2,3,3,4,4-hexadeutero-3-phenylpropyl sulfide**. To a solution of sodium thiomethoxide (0.44 g, 6.3 mmol) in dry ethanol (15 mL) under Ar, 2,2,3,3,4,4-hexadeutero-3-phenylpropyl p-toluenesulfonate (0.62 g, 2.1 mmol) dissolved in dry THF (20 mL) was added. The mixture was stirred for three hours. The mixture was poured into water (25 mL) and the aqueous layer was extracted with ether (3 x 25 mL). The combined organic layers were washed successively with brine (2 x 25 mL) and water (2 x 25 mL). The mixture was dried ($MgSO_4$) and concentrated to yield methyl 2,2,3,3-tetradeutero-3-phenylpropyl sulfide in 94% yield. $^1$H NMR ($CDCl_3$) δ 7.29-7.25 (m, 2H), 7.18-7.16 (m, 3H), 2.07 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 141.6, 128.5, 128.4, 125.9, 15.4.

**Methyl 2,2,3,3,4,4-hexadeutero-3-phenylpropyl sulfoxide (1b)** was prepared from methyl 2,2,3,3,4,4-hexadeutero-3-phenylpropyl sulfide (0.08 g, 0.05 mmol) as described above in quantitative yield. It was further purified by recrystallization from ether at low temperature yielding white crystals (65% yield). $^1$H NMR ($CDCl_3$) δ 7.28 - 7.24 (m, 2H), 7.19 - 7.13 (m, 3H), 2.49 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 140.3, 128.6, 128.5, 126.4, 38.5. EI-MS (m/e, relative abundance) 188 (38), 123 (100), 93 (54). IR (thin film): 3021, 2983, 2213, 2111, 1448, 1107, 1040, 744, 703 cm$^{-1}$.

**3-Phenylpropylsulfinyl chloride.**[116] To a round bottom flask (10 mL) diphenylpropyldisulfide (1.0 g, 0.0033 mol) and acetic acid (0.40 g, 0.0066 mol) are added and cooled to –20°C. To this solution sulfuryl chloride (1.34g. 0.0099 mol) is added dropwise with stirring over a period of 15 min. The solution was maintained at –20°C for 4h. The cold bath was then removed and the solution was allowed to warm to room temperature over a 2h period. During this time evolution of $SO_2$ and HCl is observed. To complete the reaction, the solution is warmed in a water bath to 35°C for 1h. The resulting solution is then placed on the vacuum rototary evaporator to remove acetyl chloride that was formed as a side-product during the reaction. The sulfinyl chloride was used in the next step without further purification. $^1$H NMR ($CDCl_3$) δ 7.34-7.26 (m, 2H), 7.24-7.19 (m, 3H), 3.43 – 3.33 (m, 2H), 2.86 – 2.81 (t, J = 7.2 Hz, 2H), 2.35 – 2.24 (m, 2H).

**3-Phenylpropylsulfinamide**. This method is a modification to the procedure by Chiang et al.[117] To a 3-neck round bottom flask (250 mL) equipped with a dry ice/acetone condenser and septa ammonia gas was condensed and stirred. To the liquid ammonia, 3-phenylpropyl chloride was carefully added over 30 min. as the reaction is very exothermic. After the addition was complete, the mixture was stirred for another 30 min. and the septa were removed and the excess ammonia was allow evaporate (Ar flush) in a closed fume hood for 4h. After evaporation, a yellowish solid remained. This yellowish solid was dissolved in methylene chloride and filtered and concentrated giving a yellow solid. This solid was recrystallized at low temperature from ether, giving pure product (white crystals) in 91% yield. $^1$H NMR ($CDCl_3$) δ 7.33-7.28 (m, 2H), 7.24-7.18 (m, 3H), 3.96 (broad s, 2H), 2.79 – 2.71 (m, 4H), 2.09 – 2.03 (m, 2H). EI-MS (m/e, relative abundance) 183 (10), 117 (40), 91 (100), 65 (20).

**Trifluoromethyl 3-phenylpropyl sulfide**. To an ice-cooled solution of bis(3-phenylpropyl) disulfide (1.28 g, 0.0044 mol) and trifluoromethyl trimethylsilane (1.00M in THF, 1.31 g, 0.0092 mol), maintained under Ar, was dropped, via syringe pump (1 ml/h), tetrabutylammonium

fluoride (1.00M in THF, 2.30 g, 0.0088 mol). The ice bath was removed and the reaction mixture was allowed to warm to room temperature. The mixture was stirred at room temperature for 1h. The crude mixture was deposited on top of a short silica (Silica Gel 60) column and eluted with hexane. The mixture was concentrated and gave the product (yellow oil). $^1$H NMR ($CDCl_3$) δ 7.30 – 7.26 (m, 2 H), 7.20 – 7.17 (m, 3 H), 2.73 – 2.66 (m, 4 H), 2.01 (quint, J = 14.8 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) δ 141.4, 128.5, 128.5, 126.0, 38.2, 34.4, 30.6; $^{19}$F NMR ($C_6F_6$) δ -41.3.

**Methyl Vinyl Sulfide.**[86] To a 2-neck round bottom flask equipped with two condensers, one condenser sealed with a septum and a microdistillation head. The other condenser was used as the inlet for 2-(methylthio)ethanol and argon. The microdistillation head was equipped with a round bottom flask for the sulfide trap (isopropanol/dry ice; –78°C). Both condensers and the microdistillation head were cooled with water. Argon was used to control the flow sulfide gas being formed to the trap.

To the round bottom flask was added KOH (23.5 g, o.42 mol). The KOH containing flask was heated to 320°C for 30 min. The KOH became a molten liquid that was stirred. The system was then placed under Ar, and very slowly (over 15 to 20 min.) added via syringe dropwise was 2-(methylthio)ethanol (10.6 g, 0.12 mol). Gas immediately evolved and methyl vinyl sulfide began to condense in the trap. Once all of the 2-(methylthio)ethanol was added the reaction was allowed to stir for until gas evolution stopped. The product, methyl vinyl sulfide, was pure by NMR and was produced in quantitative yields. $^1$H NMR ($CDCl_3$) δ 6.45 (dd, J = 16.4 and 10.0 Hz, 1 H), 5.20 (d, J = 10.0, 1 H), 4.96 (d, J = 16.4, 1 H), 2.26 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 132.9, 108.4, 13.6.

**Methyl Vinyl Sulfoxide (6).**[86] In a round bottom flask were placed methyl vinyl sulfide (3.0 g, 0.041 mol) and acetic acid (8.1 mL). The mixture was stirred and cooled in an ice bath and hydrogen peroxide (30%, 4.05 mL, 0.041 mol) was added dropwise. The reaction mixture was stirred for 3h, and then neutralized by slow addition of sodium carbonate until pH = 7 was reached. This mixture was then extracted with methylene chloride (5 X 80 mL). The combined organic layers were washed with water and then dried with sodium sulfate and concentrated. The concentrated product was purified by distillation (b.p =110 °C at approx. 35 mmHg). $^1$H NMR ($CDCl_3$) δ 6.68 (dd, J = 16.4 and 10.0 Hz, 1 H), 6.12 (d, J = 16.4, 1 H), 5.94 (d, J = 9.6, 1 H), 2.61 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 142.6,

121.6, 40.6. EI-MS (m/e, relative abundance) 92 (4), 90 (94), 82 (100), 80 (24). IR (neat): 3091, 3035, 3004, 2913, 1054, 963 $cm^{-1}$.

**2-Phenylethyloxirane**. To an ice-cooled, stirred solution of m-chloroperbenzoic acid (85%, 18.84 g, 0.091 mol) in methylene chloride (100 ml), 4-phenyl-1-butene (10.0 g, 0.076 mol) was added dropwise. The mixture was stirred at room temperature for 12 h. The solution was washed with 5% NaOH (2 x 50 ml) and saturated aqueous NaCl (2 x 50 ml), dried ($MgSO_4$), and concentrated to give the product in quantitative yield. $^1H$ NMR ($CDCl_3$) δ 7.33 - 7.27 (m, 2 H), 7.23 - 7.18 (m, 3 H), 2.99-2.93 (m, 1 H), 2.84 - 2.74 (m, 1 H), 2.76 (t, J = 3.9 Hz, 2 H), 2.48 (dd, J = 2.7 and 5.1 Hz, 1 H), 1.87 - 1.91 (m, 2 H); $^{13}C$ NMR ($CDCl_3$) δ 141.3, 128.5, 128.4, 126.1, 51.9, 47.3, 34.4, 32.3.

**2-Phenylethylthiirane**. Potassium thiocyanate (13.1 g, 0.14 mol) dissolved in $H_2O$ (50 ml) was added dropwise to a stirred solution of 4-phenyl-1-butene oxide (10.0 g, 0.068 mol) in 1,4-dioxane (50 ml). The turbid solution was stirred under reflux until reaction completion as monitored by GC, usually 24 h. The layers were separated and the aqueous layer was extracted with ether (3 x 50 ml). The layers were combined, dried ($MgSO_4$), and concentrated to give the product in 96% yield. $^1H$ NMR ($CDCl_3$) δ 7.33 – 7.27 (m, 2 H), 7.22 – 7.18 (m, 3 H), 2.93 – 2. 75 (m, 4 H), 2.49 (d, J = 6.3 Hz, 1 H), 2.17 (d, J = 5.7 Hz, 1 H), 1.80-1.75 (m, 1 H), $^{13}C$ NMR ($CDCl_3$) δ 141.2, 128.6, 128.5, 126.1, 38.4, 35.7, 35.5, 26.1.

**anti-2-Phenylethylthiirane S-oxide**. To a solution of 4-phenyl-1-butene thiirane (5.0 g, 0.03 mol) in methylene chloride (25 ml) at –78 °C, m-Chloroperbenzoic acid (85%, 6.31 g, 0.03 mol) in methylene chloride (25 ml) was added dropwise. Then mixture was stirred until TLC indicated completion, usually 3 h. Dry $NH_3$ was impinged on the cold solution and the precipitate was removed by suction filtration through Celite. This process was repeated until no more precipitate was formed, generally 3 times. The mixture was allowed to stand at 4 °C overnight. This allows the labile syn isomer to decompose to a thiosulfinate which can be readily separated from the desired anti isomer. After standing overnight, mixture was purified via flash chromatography on Silica gel 60 using 75% $CH_2Cl_2$/25% EtOAc as the eluent (isolated, 40% yield). The eluent was cooled (ice-bath) prior to use in the column.. $^1H$ NMR ($CDCl_3$) δ 7.31-7.18 (m, 5 H), 2.95 – 2.90 (m, 1 H), 2.84 (t, J = 7.2 Hz, 2 H), 2.66 (dd, J = 6.8 and 10.4 Hz, 1 H), 1.97 (dd, J = 6.8 and 9.6 Hz, 1 H), 1.68 (ddd, .J = 7.6, 14.8, and

22.0 Hz, 1 H), 1.59 (ddd, J = 8.4, 15.6, and 23.2 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) δ 139.8, 128.5, 128.5, 128.2, 126.3, 49.4, 41.4, 33.7, 31.1.

**Methyl (E)-4-phenyl-1-enyl sulfoxide (6a).**[85] A dry round bottom flask was charged with dry THF (10 ml) and lithium hexamethyldisilazide (1.07 g, 0.0064 mol) and was cooled to –78 °C. A solution of anti-4-phenyl-1-butenylthiirane S-oxide (1.05 g, 0.0058 mol) in cold dry THF (5 ml) was added dropwise via syringe. The mixture turned yellow and was stirred for 15 min at –78 °C. The reaction mixture was quenched by the addition of excess methyl iodide (4.12 g, 0.029 mol) in THF (10 ml). The cold bath was removed and the solution was allowed to stir at room temperature for 12 h. Aqueous ammonium chloride (25 ml) was added and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 25 ml) and the organic layers were combined, washed with saturated aqueous NaCl (50 ml), and dried ($MgSO_4$). The crude mixture was concentrated and upon flash chromatography (75% $CH_2Cl_2$/25% EtOAc as eluent) the product was obtained in 48% yield. $^1H$ NMR ($CDCl_3$) δ 7. 31 - 7.26 (m, 2 H), 7. 20 - 7.16 (m, 3 H), 6.51 (dt, J = 15.2 and 6.8 Hz, 1 H), 6.24 (d, J = 15.2 Hz, 1 H), 2.79 (t, J = 7.6 Hz, 2 H), 2.59 (t, J = 6.8 Hz, 2 H), 2.54 (s, 3 H); $^{13}C$ NMR ($CDCl_3$) δ 140.5, 139.2, 134.8, 128.5, 128.5, 126.3, 40.8, 34.5, 33.6.

**Methanesulfinyl chloride.**[118] To a mixture of dimethyldisulfide (10.5 g, 0.11 mol) and trimethylsilyl acetate (29.4 g, 0.22) chilled in an ice bath (0 °C) freshly distilled sulfuryl chloride (45.0 g, 0.33 mol) was added dropwise with stirring. After the addition had been completed, the reaction mixture was allowed to warm to room temperature. After the evolution of volatile by-products, the residue was distilled under water aspirator vacuum (88 °C) to give pure product as shown by NMR in quantitative yield. $^1H$ NMR ($CDCl_3$) δ 3.36 (s, 3H).

**3-Phenylpropyl methanesulfinate (7).**[119] A solution of methyanesulfinyl chloride (10.0 g, 0.10 mol) in dry ether (80 mL) was added dropwise with stirring and cooling in an icebath to a solution of distilled 3-phenylpropan-1-ol (12.6 g, 0.093 mol) and pyridine (8.1 g, 0.10 mol) in ether (20 mL). After the mixture was stirred overnight, the mixture was poured into ether (100 mL) and extracted with cold water (20 mL), cold HCl (10 %, 20 mL), cold saturated $NaHCO_3$ (20 mL), and cold water, in that order. The organic layer was dried ($MgSO_4$) and concentrated via rotary evaporator. The crude product (as needed in 2 mL to 3 mL aliquots) was purified using flash chromotography ($CH_2Cl_2$) affording a clear liquid. $^1H$ NMR ($CDCl_3$) δ 7.31 - 7.26 (m, 2H), 7.21 - 7.18 (m, 3H), 4.09 – 3.98 (m, 2H),

2.72 (t, J = 4.0 Hz, 2 H), 2.064 – 1.978 (m, 2H), 2.62 (s, 3H); $^{13}C$ NMR ($CDCl_3$) δ 141.0, 128.5, 128.5, 126.2, 67.5, 44.2, 31.9, 31.9. EI-MS (m/e, relative abundance) 198 (3), 118 (100), 117 (56), 91 (76). IR (thin film): 3025, 2947, 2880, 1603, 1132, 1017, 907, 744, 701 $cm^{-1}$.

**Computational Details**

All computations, except the Becke3LYP, G2 calculation on methanesulfenic acid and a few semiempirical conformational searches were carried out with the GAMESS suite of programs.[120] Results were visualized with MacMolPlt.[121] The Becke3LYP and G2 calculations were carried out using GAUSSIAN 94,[122] in which the default 6-311 basis set was made to conform with those in GAMESS, as developed by McLean and Chandler.[123] Low energy conformations of starting materials and products were determined using the PM3 model, and subsequent optimizations used those conformations as starting geometries. Hessians were obtained to confirm the nature of the stationary points. For each molecule, the coordinates, absolute energy in hartrees, and zero point energies are given in Appendix 8.

The temperature-dependent KIE for the Ei reaction was calculated using the program ISOEFF98[99], which uses vibrational frequencies from the substrate and TS to solve for the KIE using Bigeleisen equation.[100,102] The ISOEFF98 program uses hessian matrices obtained from GAMESS output.

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# CHAPTER 2

# Ei ELIMINATION: AN UNPRECEDENTED FACET OF SULFONE CHEMISTRY

Based on a paper published in the Journal of the American Chemical Society[1]

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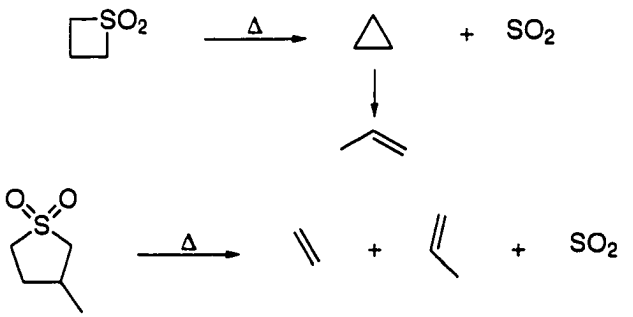
## Abstract

Thermolysis of methyl 3-phenylpropyl sulfone in the gas phase results in formation of allylbenzene. Activation parameters of $\Delta H^{\ddagger}$ = 53.5 ± 1.0 kcal/mol and $\Delta S^{\ddagger}$ = -0.7 ± 1.4 cal/mol•K were obtained over the range of 490 – 550 °C. Similar measurements with a deuterated analog show a substantial isotope effect, and a lower activation enthalpy is observed for the formation of styrene from methyl 2-phenylethyl sulfone. Along with high quality ab initio calculations of activation parameters and kinetic isotope effects, these results indicate that this is the first reported Ei reaction of a simple sulfone. However, phenyl 3-phenylpropyl sulfone does not undergo a clean Ei reaction as homolysis becomes a competing reaction.

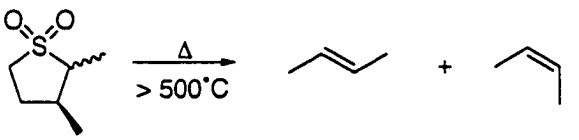
## Introduction

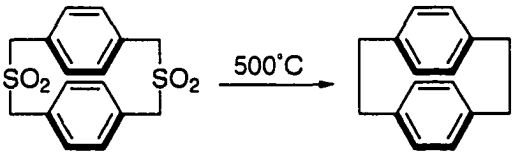
The thermolytic behavior of both structurally simple and complex sulfones has been studied for a number of years. Progress was reviewed as early as 1966.[2] Pyrolysis of sulfones usually results in the loss of $SO_2$ and the reactions are generally understood to be homolytic, electrocyclic, or chelotropic, though ionic mechanisms have been suggested on occasion.[3-5] We report here a new reaction pathway for sulfones, the Ei elimination. Though familiar from sulfoxide chemistry,[4,6-9] this reaction has only been suggested for the more highly oxidized cousin in polymer degradation.[10-12]

**Homolytic Reactions**. Kinetics of the thermal decompostion of trimethylene sulfone and 3-methyl sulfolane was investigated in toluene.[13] The thermolysis of trimethylene sulfone led to cyclopropane, propylene, and sulfur dioxide. The rate expression for the reaction was in agreement with a radical process ($k = 10^{16.1 \pm 0.3}$ exp ([-28100 ± 500]/T) $sec^{-1}$). The thermolysis of 3-methyl sulfolane yielded propylene, ethylene, and sulfur dioxide with a similar rate expression ($k = 10^{16.1 \pm 0.4}$ exp ([-33200 ± 750]/T) $sec^{-1}$). From the data, the authors concluded C-S bond cleavage followed by C-C bond homolysis in the sulfolane case and in the sulfone case, $SO_2$ ejection was assumed to occur simultaneously with cyclopropane formation after initial C-S bond cleavage.



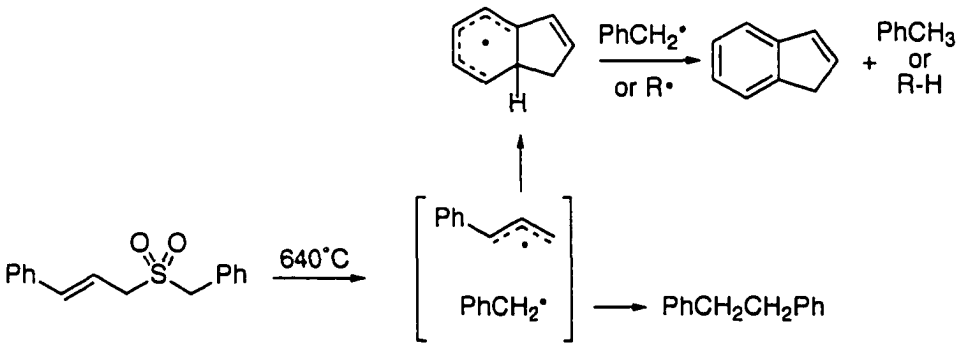

Mock and co-workers have also suggested that substituted sulfolanes decompose via diradical intermediates through product analysis.[14] Trans- and cis-2,3-dimethyl sulfolanes were subjected to thermolysis above 500°C and found to produce almost equal mixtures of trans- and cis-2-butenes regardless of the stereochemistry of the starting sulfolane. The authors do mention the possibly of a heterolytic C-S cleavage and the formation of zwitterionic intermediates which could also account for the isomerization.



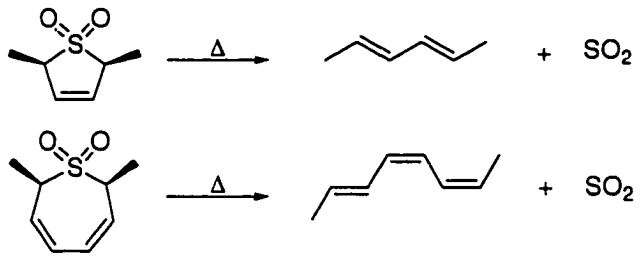



Sulfone pyrolysis in the gas phase has been used in the synthesis of macrocycles.[15] It has been proposed that the reaction occurred by C-S bond cleavage and then radical recombination to form large macrocycles such as cyclophanes.[3] Though most examples extrude only one or two $SO_2$ groups as many as four groups have been expelled at one time.[15]

The thermal reaction of cinnamyl benzyl sulfone was investigated.[16] Pyrolysis of cinnamyl benzyl sulfone at 640°C produced many products from radical recombination after extrusion of $SO_2$. The major products produced from the benzyl radical and the cinnamyl radical were styrene, indene, bibenzyl, and toulene. Indene formation was postulated to occur via internal attack of the cinnamyl radical followed by hydrogen abstraction from other radicals.

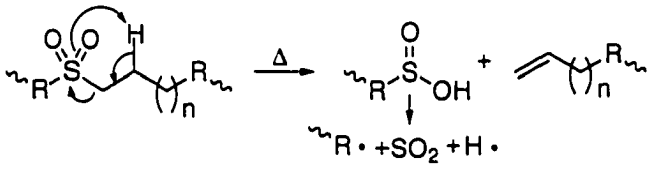



**Electrocyclic or Chelotropic Reactions.** Cheletropic reactions were defined by Woodward and Hoffmann as processes in which two sigma bonds which terminate at a single atom are made, or broken, in concert.[5] Sulfur dioxide extrusion in sulfolenes is a well known case.[17] The disrotatory (suprafacial) electrocyclic elimination of $SO_2$ from cis-2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide afforded (E,E)-2,4-hexadiene stereospecifically.[18,19] Mock also investigated the $SO_2$ elimination in cis-2,7-dimethyl-2,7-dihydrothiepin 1,1-dioxide.[20] The pyrolysis allow detection of the conrotatory (antarafacial) expulsion of $SO_2$ in production of (E,Z,Z)-2,4,6-octatriene. These pericyclic $SO_2$

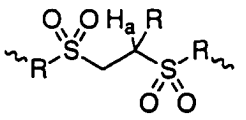


extrusion reactions occur at much lower temperatures (~250°C and below) than the above homolytic reactions.

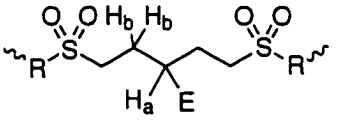
**Polymer Degradation.** In 1964, Wellisch and co-workers evaulated the thermolysis of $C_4$, $C_6$, and $C_8$ polymethylene sulfones at 275°C, under pressure for one hour.[12] Many products were produced from the thermolysis and olefins were formed in the majority. The authors postulated a mechanism where the initiation step is the Ei elimination followed by the sulfinic acid decomposing homolytically. The acid decomposition was used to account for the slew of products formed. Later the same group suggested the Ei reaction again but never ruled out the C-S cleavage reaction as shown in Scheme 1.[11]



Schmidt-Winkel and Wudl studied the degradation of polysulfones using thermogravimetric analysis.[10] Although it was not stated implicitly in the paper, polysulfones (e.g. polysulfone **A**) that contained an acidic β-proton decomposed at lower temperatures. Polysulfones (e.g. polysulfone **B**) containing less acidic β-protons were able to withstand much higher temperatures before decomposition occurred. Wudl argued that polysulfone **A** should be more stable since **A** had fewer β-hydrogens than polysulfone **B** if the Ei mechanism is operative. The authors also stated the Ei elimination could be operative with **A** and that **B** is decomposing via C-S cleavage. These results are



A

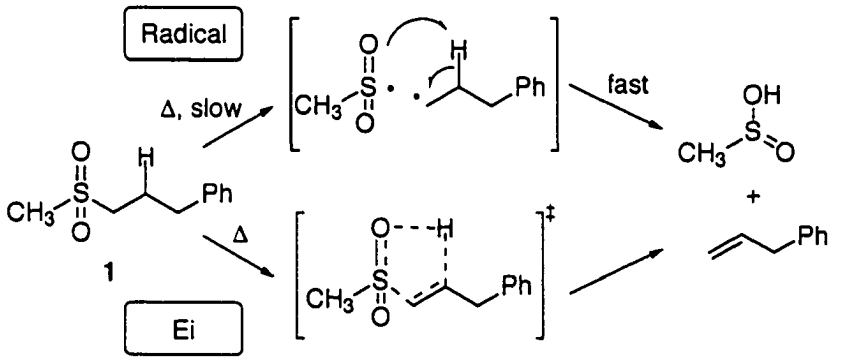


B

consistent our results with sulfoxides from Chapter 1 (i.e. a lower activation barrier is observed with sulfoxides that contain acidic β-hydrogens).

**Present Investigation.** Two limiting mechanisms for the formation of allylbenzene from **1**, homolytic and Ei, may be envisioned, as illustrated in Scheme 1. Ei elimination postulates that the sulfone group acts simultaneously as base and leaving group.[21] Sulfinates are well known leaving groups in E2 and $E1_{cb}$ reactions.[22-27] However, sulfones are considerably less basic than sulfoxides. The proton affinity of dimethyl sulfone is a full 17 kcal/mol less than that of dimethyl sulfoxide.[28] It is thus imperative to demonstrate the plausibility of the sulfone Ei reaction by means other than analogy. Below are presented results from gas phase activation data, kinetic isotope effects, and ab initio computations that all strongly support the concerted elimination of sulfinic acids from unactivated alkanes to give olefins.

**Scheme 1.**




# Results

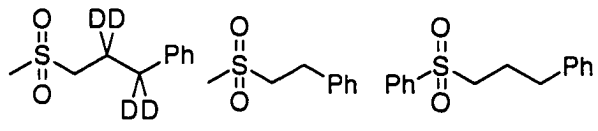
**Experimental Results.** Pyrolysis of sulfones **1-4** was carried out in a temperature controlled pulsed stirred-flow reactor (SFR) with He carrier gas that feeds into a GC.[29] Allylbenzene was observed from **1**, **2**, **4**, and styrene from **3**. Methanesulfinic acid was not detected directly; its

presence was inferred. Activation parameters for the formation of olefins from sulfones **1**, **2**, **3**, and **4** are given in Table 1.

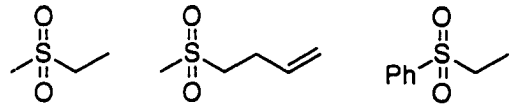
**Table 1.** Experimental Activation Parameters.[a]

| Compound | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $E_a$ | log A |
|---|---|---|---|---|
| **1** | 53.5 ± 1.0 | -0.7 ± 1.4 | 55.0 ± 1.0 | 13.5 ± 0.4 |
| **2** | 52.5 ± 1.6 | -3.2 ± 2.0 | 54.0 ± 1.6 | 12.9 ± 0.4 |
| **3** | 47.0 ± 1.8 | -6.8 ± 2.4 | 48.5 ± 1.8 | 12.2 ± 0.6 |
| **4** | 46.9 ± 2.6 | -9.7 ± 3.3 | 48.5 ± 1.8 | 11.5 ± 0.8 |

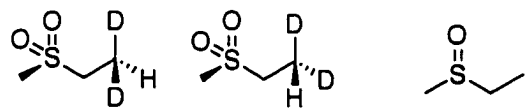
[a] $\Delta H^{\ddagger}$ and $E_a$ values expressed in kcal/mol; $\Delta S$ in cal/mol•K; log A in $sec^{-1}$. Errors are expressed as the 95% confidence limits.



**2** **3** **4**



**5** **6** **7**

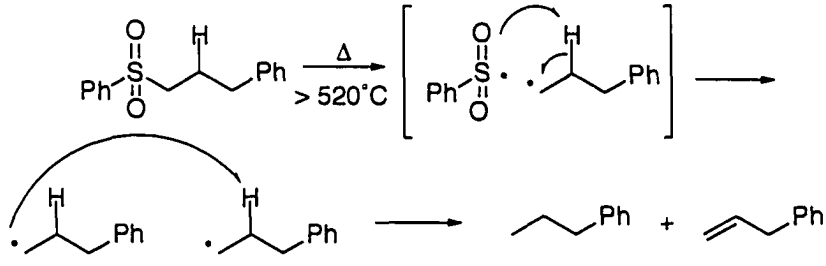


**8** **9** **10**

The residence time in the hot zone of the quartz reactor is individually calibrated and is of the order of a few seconds. Temperature regions for data collection are limited to where both starting material and product can be accurately quantified from the GC run of a single reaction on that time scale. Thus the data for **1** and **2** were collected over the range of 490 - 550 °C. Data for **3** and **4** were collected over the range of 450 – 500 °C and 500 – 550 °C, respectively. Arrhenius and Eyring plots are presented for sulfones **3** and **4** in Appendix 1, Figures 5 and 6, respectively.

In contrast to **1**, **2**, and **3**, thermolysis of **4** was not clean above 520 °C. Below 520 °C, allylbenzene is the only product produced. At 520°C three other products were observed. Only one

of them was identified, because we were limited to GC co-injection as an analytical method. The identified compound was propylbenzene. At the final temperature (550 °C) from the peak areas, the thermolyzed compostion was allylbenzene (28%), propylbenzene (8%), other products (8%), and **4** (56%). The formation of propylbenzene can be explained by the homolysis of the C-S bond followed by hydrogen abstraction by the carbon-centered radical as shown below.




The temperature dependent kinetic isotope effect (KIE) for **1** vs. **2** was evaluated by successive injections of **1** and **2** into the SFR on the same day using the same reactor cell to insure greatest accuracy. A $k_H/k_D$ of 2.0 ± 0.2 was observed over the whole range, as shown in Figure 1.

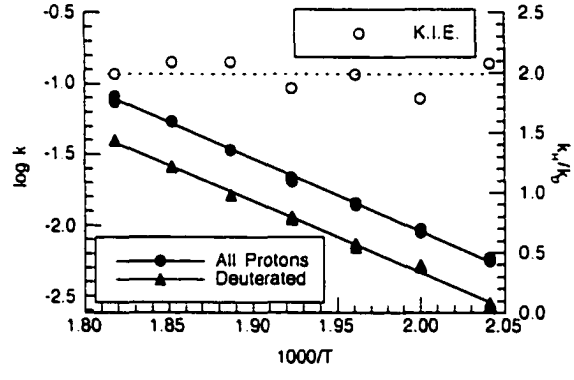



**Figure 1.** Kinetic data for the elimination reaction of **1** and **2**

**Computational Results.** Model compounds **5**, **6**, and **7** were examined using ab initio methods. Activation enthalpies and heats of reaction including zero point energies are shown in Table 2. In a similar detailed experimental and computational study to be presented in Chapter,[30] it was determined that MP2/6-311+(3df,2p)//MP2/6-31G(d,p) calculations accurately reproduced

activation parameters of sulfinyl Ei reactions, and this level of theory was applied here. The transition states (TS) for **5**, **6**, and **7** are illustrated in Figure 2. All are simililar in structure.

**Table 2.** Calculated Activation Barriers and Heats of Reaction.[a]

| Compound | $\Delta H^{\ddagger}$ | $\Delta H$ | $\Delta H_{est}$ [b] |
|---|---|---|---|
| **5** | 54.5 | 35.7 | 35.3 |
| **6** | 50.6 | 28.3 | 28.6 |
| **7** | 54.8 | 38.3 | |
| **10** | 32.3 | 22.6 | |

[a]Calculated enthalpies at MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) include appropriately scaled zero point energies. All enthalpies are in kcal/mol. [b] $\Delta H_{est}$ is estimated from $\Delta H_f$ Benson-type values for **4** and **5**, experimental values for ethylene and butadiene, and a G2 calculation for $CH_3SO_2H$.[31-33]

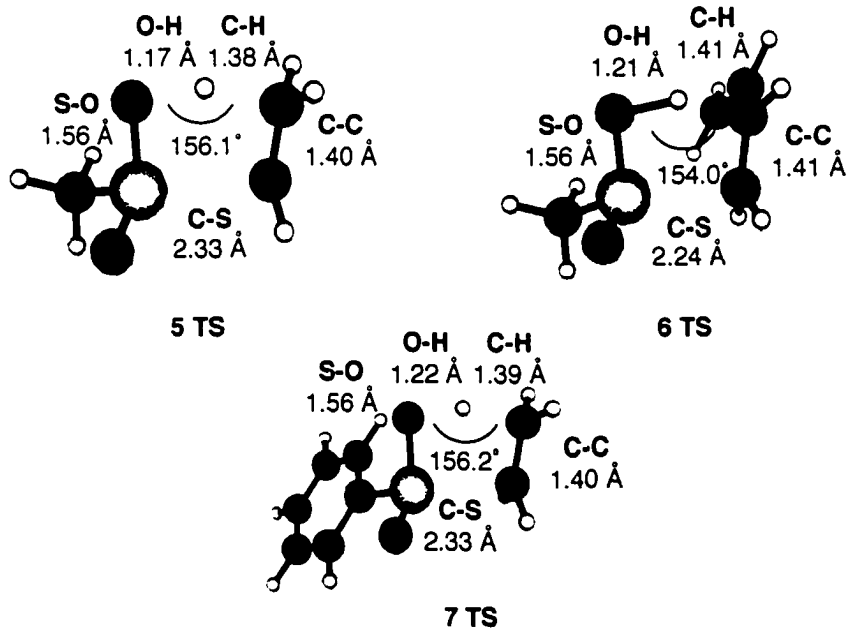



**Figure 2.** Transition state geometries calculated at MP2/6-31G(d,p)

CASSSF/6-31G(d,p) calculations were also carried out on the TS of **5**, and were consistent with a single-configuration closed-shell TS as shown by the natural orbitial occupation numbers being basically filled or empty. The active space for these calculations consisted of 6 electrons in 5 orbitals and the natural orbital occupation numbers for the active space are: 1.975, 1.973, 1.999, 0.027, and 0.026. The input orbitals in the transition state correlated to the C-S $\sigma$ and $\sigma^*$ orbitals, the C-H $\sigma$ and $\sigma^*$ orbitals, and a lone pair on O in the starting material. The correlation to the product was to the C-C $\pi$ and $\pi^*$ orbitals, OH $\sigma$ and $\sigma^*$ orbitals, and a lone pair on sulfur.

The temperature-dependent KIE for the Ei reaction was calculated[34] using the program ISOEFF98,[35,36] which uses vibrational frequencies from the substrate and its respective TS to solve for the KIE using the Bigeleisen equations.[37-39] The KIE was calculated for conformers **8** and **9** of dideuterated **5** at 298 K (5.02 and 4.74, using unscaled and scaled vibrational frequencies, respectively) and in the temperature range of the experiments, 763 – 823 K (1.95-1.86 and 1.90-1.82, unscaled and scaled vibrational frequencies, respectively). The calculated KIE is in agreement with the experimental KIE (2.0 ± 0.2).

## Discussion

The compounds used in this experimental and computational study were chosen to distinguish between homolytic and Ei mechanisms. The homolytic path does not predict a significant activation enthalpy difference between **1** and **3** because C-S cleavage is certainly rate limiting. Yet, a 6.5 kcal/mol difference is observed (Table 1), consistent with partial formation of the olefin in the TS. Further, the observed $\Delta S^{\ddagger}$ values do not appear consistent with a homolysis reaction.

Computational models **5** and **6** were used to gauge expectations for the difference in activation enthalpies for **1** and **3**. The calculated $\Delta H^{\ddagger}$ values for **5** and **6** are within reasonable expectations of the experimental values for **1** and **3**. The 4 kcal/mol deviation for **3/6** is the largest we have observed using this level of theory and similar molecular simplification on sulfonyl and sulfinyl elimination reactions.[30] Nonetheless the experimentally observed change of about 6.5 kcal/mol is consistent with expectations for the Ei reaction, borne out by the 3.9 kcal/mol difference in the model compound calculations.

Compounds **1** and **2** also support the Ei mechanism in that a significant KIE is not predicted for the radical pathway. Both primary and secondary KIEs are expected for the Ei reaction, and the large primary KIE should be observable even at elevated temperatures.

An isotope effect is indeed observed, as illustrated in Figure 1. Table 1 illustrates the limits of the precision of the current data, obtained under a fairly narrow temperature region. The activation enthalpy for **2** is not expected to be lower than that of **1**, and it should be noted that there is significant overlap of the ranges within the reported error bars. (Based on ZPE differences for the isotopomers, the dideuterated compound should have a 0.9 kcal/mol higher $\Delta H^{\ddagger}$.) Over the entire range of data, a $k_H/k_D$ of 2.0 ± 0.2 was observed experimentally for **1** vs. **2** (Figure 1). The KIEs calculated for Ei elimination of **8** and **9** vs. **5** to give deuteroethylene are from 1.90 to 1.82 over this same temperature range. Inspection of Figure 1 reveals that the data scatter does not allow observation of a KIE change of <5% over the temperature region, and the dotted line is arbitrarily plotted at the average value, 2.0. Given the limitations of the experimental data and the necessity to reduce the size of the molecule for computations, the calculated and experimental KIEs are taken to be in excellent agreement.

The magnitude of $\Delta H^{\ddagger}$ for the sulfone Ei reaction is significantly greater than that for the corresponding sulfoxide elimination. The activation entropies in Table 1, however, are in line with literature reports and our observations for the sulfoxide reaction.[30] The calculated $\Delta H$ and $\Delta H^{\ddagger}$ for sulfoxide **10** are included in Table 2 for comparison. Neither the sulfoxide nor the sulfone reaction has a transition state that can be described as particularly early or late. The computed transition state geometries are substantially similar, save that both the C-H and H-O distances are 0.02-0.03 Å shorter at the expense of a 0.05 Å longer C-C distance for **5**, compared to the sulfoxide **10**. Both have all 5 key atoms in a nearly coplanar arrangement.

A final experimental consideration is the observed value of $\Delta H^{\ddagger}$, which is inconsistent with the radical mechanism. The C-S bond dissociation energies (BDEs) of sulfones **1-3** are expected to be approximately 68 kcal/mol,[40,41] significantly higher than the observed $\Delta H^{\ddagger}$ of 53.5 kcal/mol. In contrast, the C-S bond dissociation energy for sulfone **4** is expected to be 54 kcal/mol and indeed the results are consistent with competition between an Ei reacton and homolysis. Computationally

sulfone **4** was predicted to undergo the Ei reaction with a barrier of 54 kcal/mol but experimentally a much lower value (46 kcal/mol) was observed. The fact that computationally the elimination barrier is the predicted to be the same as the C-S bond strength indicates that the reactions presented in Scheme 1 will be competitive. The disagreement between the experimental and theoretical values could arise from secondary reactions during thermolysis producing allylbenzene from both Ei and radical reactions.

A large part of the difference in $\Delta H^{\ddagger}$ as compared to the sulfoxide elimination may lie simply in the fact that the sulfone reaction is substantially more endothermic. It is also attractive to speculate that the decreased basicity of the sulfonyl group relative to the sulfinyl group outweighs the increased nucleofugacity in the transition state. While studies that compare nucleofugacity are generally system dependent, we have been unable to find any cases in which sulfones are any more than modestly better leaving groups than the corresponding sulfoxide.[25-27]

Finally, given the strong evidence for the Ei reaction of sulfones, one must ask why this simple thermolytic reaction has escaped the attention of the chemical community except for the proposal in the one polymer instance. First, the activation enthalpy is not insubstantial. Many sulfones that have been pyrolyzed at sufficiently high temperatures for the Ei reaction to be observed are not physically capable of the reaction or have substituents that lower a C-S bond dissociation energy such that it is in the range of the $\Delta H^{\ddagger}$ reported here. Not only are the BDEs for benzyl- and allyl-$SO_2R$ bonds low (55-56 kcal/mol), but the $CH_3$-$SO_2Ph$ BDE is reported to be 54-57 kcal/mol.[40,41] Such weak bonds would probably make homolytic reactions very competitive, especially considering the favorable $\Delta S^{\ddagger}$ values for the homolyses. This competitiveness was shown with our results with the thermolysis of phenyl 3-phenylpropyl sulfone **4**. Cyclic compounds may not have revealed Ei reactivity because the reverse reaction is likely to be very rapid, with sulfone being overwhelmingly favored thermodynamically.

## Conclusions

In summary, a new unimolecular reaction of sulfones, Ei elimination to form alkenes, has been observed. Its activation enthalpy, though high, is below what is to be expected for C-S bond rupture. The radical mechanism further is ruled out with alkyl sulfones **1**, **2**, and **3** on grounds of

substituent effects and computations of an Ei transition state that well reproduces the absolute $\Delta H^{\ddagger}$ and KIE. Aryl sulfone **4** gave evidence for the Ei reaction competing with homolysis.

# Experimental Section

## Instrument

The stirred-flow reactor has a temperature controlled furnace and is modeled very closely after the one that has been previously described.[29] It uses He as a carrier gas to bring the sample into a reactor whose volume controls the residence time, which is a few seconds. Samples were injected as concentrated solutions in acetonitrile. After the furnace section, the gases are sent to a GC that operates at lower temperatures, where starting materials and products are separated and quantified. Rate constants are extracted from each run, and multiple injections were made at each temperature. For the isotope effect measurements, the samples **1** and **2** were measured alternately at each temperature to insure accurate measurements of $k_H/k_D$. All sulfones thermalized were greater than 99% purity, as determined by the observation of a single peak by GC without thermolysis.

### Compound preparation

**General.** Unless otherwise noted, starting materials were obtained from Aldrich and used as received. Characterization was carried out on a Bruker Avance DXR NMR operating at 400 MHz for proton and 100 MHz for carbon. The $^{13}C$ signals for $CD_2$ carbons were generally not observed due to the low signal-to-noise and high multiplicity. MS were obtained on a Finnigan TSQ 700 operating in EI mode. IR spectra were obtained on a Mattson Galaxy Series FTIR 3000. Dry THF was freshly distilled from benzophenone ketyl. Both compounds **1** and **3** are known;[42-44] the isotopomer **2** is a new compound. Modern spectroscopic data for **1** and **2**, both prepared by oxidation sulfoxides already on hand,[45] are in the supplementary material.

**General procedure for preparation of sulfone from sulfide (or sulfoxide).** To an ice cooled solution of 2-3 mmol of the sulfoxide (sulfide) in methylene chloride (15 mL) was added 1.1 (2.2) equivalents of m-chloroperbenzoic acid dissolved in 25 mL methylene chloride dropwise by means of a dropping funnel. After two hours, the mixture was poured in to aqueous NaOH (5%, 50

mL) and the layers were separated. The organic layer was washed with another portion of aqueous NaOH, then dried with $MgSO_4$ and concentrated in vacuo. Yields were nearly quantitative and products clean by NMR. Further purification was carried out as noted.

**Methyl 3-phenylpropyl sulfone** (1) was prepared by oxidation of methyl 3-phenylpropyl sulfoxide[45] as described in the main text. It was further purified by recrystallization from ether at low temperature. $^1H$ NMR ($CDCl_3$) δ 7.29 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 2H) 2.98-2.94 (m, 2H, distorted triplet), 2.83 (s, 3H), 2.76 (t, J = 8.0 Hz, 3H), 2.19-2.12 (m, 2H, distorted quintet); $^{13}C$ NMR ($CDCl_3$) δ 139.8, 128.8, 128.5, 126.6, 53.9, 40.6, 34.2, 24.0. EI-MS (m/e, relative abundance) 198 (18), 117 (100), 91 (37). IR (thin film): 3008, 2929, 2873, 1315, 1124, 754, 704 $cm^{-1}$. Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12; S, 16.17. Found: C, 60.44; H, 7.21; S, 15.96.

**Ethyl 2,2,3,3-tetradeutero-3-phenylpropionate**. In a 250 mL round bottom flask, ethyl phenylpropiolate (10.0 g, 57.4 mmol) was dissolved in diethyl ether (10 mL) and Pd/C (2.0 g) was added. The mixture was stirred rapidly and $D_2$ was introduced into the chamber as follows: a three-way valve was attached to the deuterium source, the reaction flask, and a calibrated U-shaped tube (1.4 L) filled with mineral oil. The reaction was run until completion as monitored by GC. The mixture was filtered and concentrated to give the product in 86% yield. The product was clean by NMR and used for subsequent steps. $^1H$ NMR ($CDCl_3$) δ 7.3 -7.18 (m, 5H), 4.13 (q, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H); $^{13}C$ NMR ($CDCl_3$) δ 173.2, 140.7, 128.7, 126.4, 60.6, 14.4. IR (thin film) 3026, 2981, 2222, 2101, 1732, 1268, 1026, 735, 699 $cm^{-1}$.

**2,2,3,3-tetradeutero-3-phenyl-1-propanol**. To a suspension of lithium aluminum hydride (0.63 g, 16.5 mmol) in dry THF (25 mL) under Ar at O °C, ethyl 2,2,3,3-tetradeutero-3-phenylpropionate (1.0 g, 5.49 mmol) was added. The suspension was allowed to warm to room temperature. After stirring one hour the reaction mixture was heated to reflux for five hours. The reaction was quenched by slow, successive addition of $H_2O$ (0.6 mL), aq. NaOH (0.6 mL), and $H_2O$ (1.8 mL). The solution was filtered then poured into ether (30 mL) and washed with brine (3 x 25 mL). The organic layer was dried ($MgSO_4$) and concentrated to give 2,2,3,3-tetradeutero-3-phenyl-1-propanol in 98% yield. The material was clean by NMR and used in the next step without further

purification. $^1$H NMR ($CDCl_3$) δ 7.29-7.16 (m, 5H) 3.65 (s, 2H), 1.64 (s, 1H) $^{13}$C NMR ($CDCl_3$) δ 141.8, 128.5, 128.5, 125.9, 62.2. IR (thin film) 3346, 3024, 2918, 2876, 2206, 2112, 1604, 1043, 699 cm$^{-1}$.

**2,2,3,3-tetradeutero-3-phenylpropyl p-toluenesulfonate**. In a round bottom flask (50 mL), 2,2,3,3-tetradeutero-3-phenyl-1-propanol (0.7 g, 5.0 mmol) was dissolved in chloroform (10 mL) and cooled in an ice bath (0° C). To the solution, pyridine (0.8 g, 10.0 mmol) was added, followed by p-toluenesulfonyl chloride (1.4 g, 7.5 mmol). The reaction was monitored by TLC and completed after stirring 2.5 h. To the mixture, ether (30 mL) and water (15 mL) were added and the layers were separated. The organic layer was washed successively with HCl (2N, 20 mL), $NaHCO_3$ (5%, 20 mL), and water (25 mL). The solution was dried ($MgSO_4$) and concentrated. Flash chromatography (75/25 Hexane/EtOAc ) was use to obtain a clean sample in 71% isolated yield. $^1$H NMR ($CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.22 (t, J = 7.2 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 7.2 Hz, 2H), 4.01 (s, 2H), 2.43 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 144.8, 140.3, 133.1,129.9, 128.5, 128.5, 128.0, 126.2, 69.6, 21.7. IR (thin film) 3060, 2985, 2209, 2118, 1598, 1356, 1177, 919, 663 cm$^{-1}$.

**Methyl 2,2,3,3-tetradeutero-3-phenylpropyl sulfide**. To a solution of sodium thiomethoxide (0.3 g, 4.0 mmol) in dry ethanol (15 mL) under Ar, 2,2,3,3-tetradeutero-3-phenylpropyl p-toluenesulfonate (0.39 g, 1.3 mmol) dissolved in dry THF (20 mL) was added. The mixture was stirred for three hours. The mixture was poured into water (25 mL) and the aqueous layer was extracted with ether (3 x 25 mL). The combined organic layers were washed successively with brine (2 x 25 mL) and water (2 x 25 mL). The mixture was dried ($MgSO_4$) and concentrated to yield methyl 2,2,3,3-tetradeutero-3-phenylpropyl sulfide in quantitative yield. $^1$H NMR ($CDCl_3$) δ 7.29-7.24 (m, 2H), 7.20-7.15 (m, 3H), 2.48 (s, 2H), 2.08 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 140.8, 128.5, 128.4, 125.9, 33.4, 15.5. IR (thin film) 3059, 3024, 2914, 2205, 2101, 1603, 909, 733, 700 cm$^{-1}$.

**Methyl 2,2,3,3-tetradeutero-3-phenylpropyl sulfone** (**2**) was prepared from methyl 2,2,3,3-tetradeutero-3-phenylpropyl sulfide (0.2 g, 1.2 mmol) as described above in quantitative yield. It was further purified by recrystallization from ether at low temperature. $^1$H NMR ($CDCl_3$) δ 7.31-7.15 (m, 5H), 2.95 (s, 2H), 2.84 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 139.7, 128.8, 128.5, 126.6, 53.7, 40.6. EI-MS (m/e, relative abundance) 202 (26), 120 (100), 93 (48). IR (thin film): 3019, 2198, 2160, 2102, 1305,

1133, 744, 704 $cm^{-1}$. Anal. Calcd for $C_{10}H_{12}D_2O_2S$: C, 59.37; H, 6.98; S, 15.85. Found: C, 59.21; H, 7.12; S, 15.81, assuming D analyzes as H.

**Methyl 2-phenylethyl sulfone** (**3**) was prepared by oxidation of methyl 2-phenylethyl sulfoxide as given above. It was purified by low temperature recrystallization from ether. $^1H$ NMR ($CDCl_3$) δ 7.32 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2H), 3.30-3.26 (m, 2H, distorted triplet), 3.17-3.16 (m, 2H, distorted triplet), 2.80 (s, 3H); $^{13}C$ NMR ($CDCl_3$) δ 137.4, 129.0, 128.5, 127.2, 56.2, 41.1, 28.6. EI-MS (m/e, relative abundance) 184 (10), 104 (100), 91 (4), 77 (14). IR (thin film): 3026, 2981, 2926, 1311, 1119, 781, 723 $cm^{-1}$.

**Phenyl 3-phenylpropyl sulfone (4)** was prepared[46] by oxidation of phenyl 3-phenylpropyl sulfide as given above. It was purified by low temperature recrystallization from ether. $^1H$ NMR ($CDCl_3$) δ 7.90 – 7.86 (m, 2H) 7.68 – 7.63 (m, 2H) 7.58 – 7.53 (m, 2H), 7.30 – 7.17 (m, 4H), 7.11 – 7.09 (m, 2H), 3.10 - 3.05 (m, 2H, distorted triplet), 2.70 (t, J = 7.5 Hz, 2H), 2.10 – 1.99 (m, 2H); EI-MS (m/e, relative abundance) 260 (42), 118 (100), 91 (21). IR (thin film): 3060, 3026, 2944, 2864, 1600, 1295, 1146, 750, 701 $cm^{-1}$.

## Computational Details

All computations, except the G2 calculation on methanesulfinic acid and a few semiempirical conformational searches were carried out with the GAMESS suite of programs.[47] Results were visualized with MacMolPlt.[48] The G2 calculation was carried out using GAUSSIAN 94,[49] in which the default 6-311 basis set was made to conform with those in GAMESS, as developed by McLean and Chandler.[50] Low energy conformations of **5**, **6**, **7**, **10**, and methanesulfinic acid were determined using the PM3 model, and subsequent optimizations used those conformations as starting geometries. Hessians were obtained to confirm the nature of the stationary points. For each molecule below, the coordinates, absolute energy in hartrees, and zero point energies are given in the supplementary material.

CASSCF/6-31G(d,p) calculations were carried out on the transition state for **5**. The active space consisted of 5 orbitals with 6 electrons as described in the main text. Optimization was begun from the MP2/6-31G(d,p) geometry and did not result in substantial changes. The natural orbital

occupations were very close to 2 or 0. Appendix 9 contains the final coordinates and the precise occupations of the natural active space orbitals.

The temperature-dependent KIE for the Ei reaction was calculated[34] using the program ISOEFF98,[35,36] which uses vibrational frequencies from the substrate and TS to solve for the KIE using Bigeleisen equation.[37-39] The ISOEFF98 program uses hessian matrices obtained from GAMESS output. Appendix 9, Table 3 contains the calculated KIE for both unscaled and scaled vibrational frequencies for **8** and 9. The numbers reported in the text are averages of the KIE calculated for **8** and **9**.

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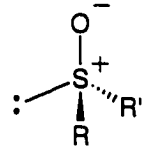
# CHAPTER 3

# COMPUTATIONAL STUDIES OF THE GROUND AND EXCITED STATE POTENTIAL OF DMSO AND $H_2SO$: RELEVANCE TO PHOTOSTEREOMUTATION

In the style of a paper to be submitted to the Journal of Physical Chemistry

## Introduction

Racemization or stereomutation of sulfoxides was first realized in the 19th century by Krafft and Lyons[1] and first reviewed in 1967 by Mislow.[2] A sulfoxide is chiral as long as it contains two different substituents at sulfur, in addtion to the oxygen atom and the lone pair of electrons. The ease of preparation[3,4] and stability[5-7] of optical active sulfoxides makes them very attractive to synthetic chemists in preparing biologically interesting compounds.[8] The stability has allowed chiral sulfoxides to function as chiral auxiliaries in organic synthesis.[9]




The fact that the pyramidal structure of sulfoxides retains its configurational integrity has generated much curiosity in finding conditions for which it undergoes racemization. This introduction considers the details of mechanisms deduced throughout the years for racemziation or stereomutation for both thermal and photochemical processes. This dissertation chapter is concerned with computation details of photoracemization along with computing ground state barriers

for thermal racemization for DMSO and $H_2SO$. It is hypothesized that racemization occurs from a vertically excited state of the sulfoxide that can relaxed to some new excited state geometry. Then this relaxed excited state geometry can subsequently fall back down to the ground state, partitioning to (+)- and (-)-sulfoxides. A simplified diagram of this is shown in Figure 1. The excited state geometries, previously unknown, will be compared to ground state geometries. Consideration of experimental facts presented in this introduction will be taken into account and where applicable comparisons of computational results with experimental results will be made.

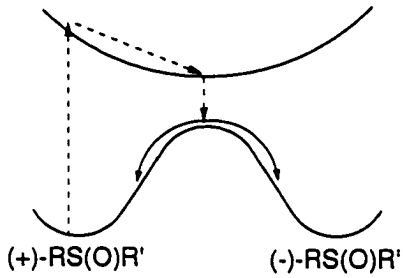
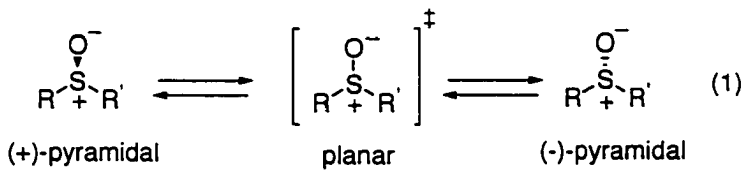


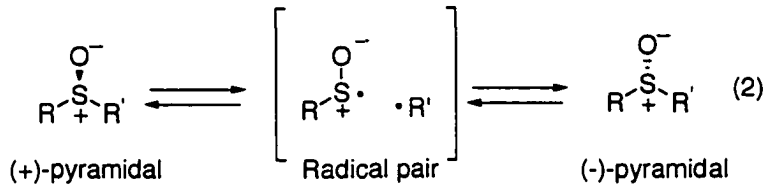

**Figure 1.** Simplified diagram for photoracemization

## Thermal Stereomutation[2]

There are three different possible unimolecular mechanisms that are known operate for the thermal inversion or stereomutation at sulfur in sulfoxides. The mechanisms for stereomutation of sulfoxides are pyramidal (vertex) inversion, C-S bond cleavage, and sigmatropic rearrangement as shown in equations 1, 2, and 3, respectively. A fourth mechanism possible for sulfoxide inversion, edge inversion, has been invoked in the inversion of phosphorus compounds but has not been observed in sulfoxides to the best of our knowledge (equation 4).[10] It is generally understood that pyramidal inversion is the "default" mechanism unless structural features facilitate either homolysis or sigmatropic chemistry.




(1)

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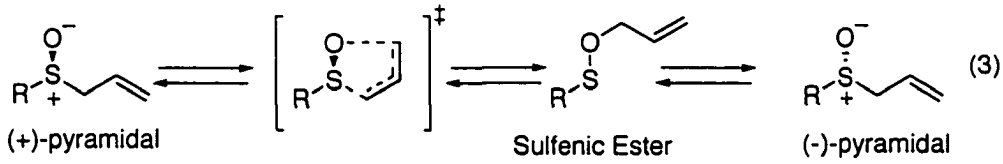
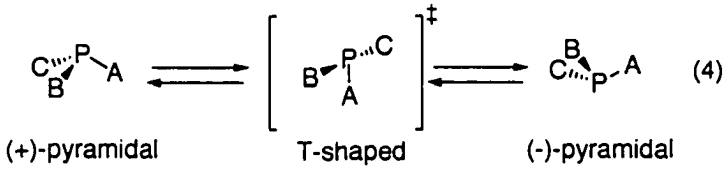



(3)




(4)

**Pyramidal Inversion**. The inversion process known as pyramidal or vertex inversion has been extensively studied by Mislow and co-workers.[5,6] This process is depicted in equation 1, where pyramidal sulfoxides flatten out through molecular vibrations to a locally planar transition state and then collapse to back to either pyramidal structure. It is a prerequisite that C-S bond cleavage does not occur and the structure does not contain a β-hydrogen to the sulfinyl group because the elimination chemistry occurs with somewhat lower activation parameters. As investigated in Chapter 1 of this dissertation, sulfoxides that contain β-hydrogens eliminate to form olefins when thermolyzed ($\Delta H^{\ddagger}$ = 30 – 33 kcal/mol for simple sulfoxides).

For diaryl, alkyl aryl, and dialkyl sulfoxides, rate constants and activation parameters were determined for the pyramidal inversion process.[6] The rate constants for inversion were relatively invariant to substituents at sulfur. The first order rate constant of racemization is about 3 X $10^{-5}$ $sec^{-1}$ in p-xylene at 210°C for all diaryl and most alkyl aryl sulfoxides. It remained within one order of magnitude for dialkyl sulfoxides. Substituent effects with diaryl sulfoxides were probed and the rate of inversion was still relatively unaffected. Activation energies were also fairly insensitive and all fell with in 7 kcal/mol of each other ($\Delta H^{\ddagger}$ = 35 – 42 kcal/mol). For selected sulfoxides, Eyring parameters for

**Table 1**. Activation Parameters for Sulfoxides p-$MeC_6H_4S(O)R$

| R | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|
| 2,4,6-$Me_3C_6H_2$[a] | 35.4 | 1.3 |
| 2-$MeC_6H_4$[a] | 36.6 | -2.8 |
| $C_6H_5$[a] | 36.2 | -5.1 |
| 1-Adamantyl[a] | 42.0 | 3.8 |
| Me[a] | 37.4 | -8.0 |
| $PhCH_2$[b] | 43.0 | 24.6 |
| $CH_2$=$CHCH_2$[c] | 23.1 | -4.9 |

[a]reference 6, [b]reference 7, [c]reference 12

inversion are shown in Table 1. Brower and Wu quantified the mechanism of pyramidal inversion by determination of the volume of activation, approximately 0 ml/mol for two diaryl sulfoxides studied.[11]

The pyramidal inversion barriers for sulfoxides have been calculated for DMSO, $F_2SO$, and $H_2SO$.[13] The inversion activation barrier for DMSO was calculated to be 48 kcal/mol at the MP2/6-31+G(2d) level of theory, for $F_2SO$ was calculated to be 39 kcal/mol at MP2/6-311+G(2d) level of theory, and for $H_2SO$ was calculated to be 40 kcal/mol at the MP2/6-311G+G(2d,p) level of theory. Higher levels of perturbation theory were employed on $F_2SO$ and $H_2SO$ only producing slightly different energy barriers.

In another pyramidal inversion study, the inversion barriers of derivatives of thiophene 1-oxide and 1,2,5-thiadiazole 1- oxide were determined experimentally[14] and computationally (Table 2).[15] Since this was completed early in the 1980s, Hartree-Fock (HF) theory with the now less used 4-31+G(d) basis set was used. The authors noted that in order to get correct description extra d polarization functions were necessary for the sulfoxide moiety. Experimentally it was determined that

**Table 2**. Inversion Barriers (kcal/mol)

| Sulfoxide | HF/4-31+G(d) | Observed |
|---|---|---|
| $H_2SO$ | 43.2 | |
| DMSO | 51.4 | 36-42[a] |
| $(NH_2)_2SO$ | 66.5 | |
| Thiophene oxide | 19.6 | 14.8[b] |
| Thiadiazole oxide | 31.9 | 33 |

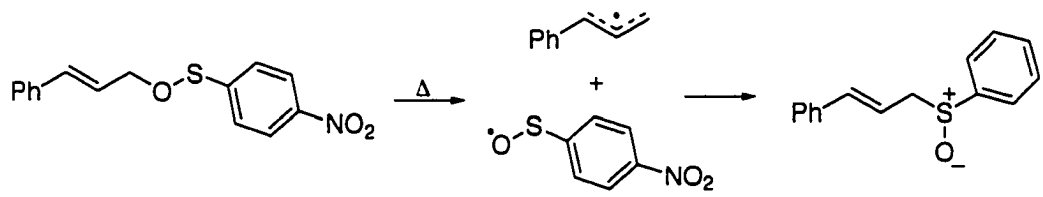
[a]Refers to alkyl sulfoxides, see reference 6 [b]reference 14

thiophene oxide and thiadiazole oxide had much lower inversion barriers than ordinary disubstituted sulfoxides due to aromaticity of the planar transition state. The barriers for inversion were determined and are shown in Table 2. To access the effects of nitrogen substituted to sulfur $(NH_2)_2SO$ was computed and compared to DMSO (see Table 2).

**C-S Bond Cleavage.** Thermolysis of benzyl p-tolyl sulfoxide took a different route to inversion than the diaryl, aryl alkyl, and dialkyl sulfoxides.[7] Pyramidal inversion of diaryl, aryl alkyl, and dialkyl sulfoxides took place at relatively high temperatures (190 – 200°C) where as benzyl p-tolyl sulfoxide stereomutated at a much lower temperature range (130 – 150°C). This was attributed to cleavage of the much weaker benzylic C-S bond (equation 2). Stereomutation occurred with much decomposition. The major decomposition products were bibenzyl and p-tolyl p-toluenethiosulfonate, recombination products of the escaped radicals. The activation parameters for stereomutation are presented in Table 1. The activation enthalpy is not notably different from the pryamidal inversion mechanism but the activation entropy (+ 25 eu) puts the nail in the coffin in favor of the radical mechanism. The additional information from the activation enthalpy is the upper bound for the benzyl C-S bond strength of 43 kcal/mol.

**Sigmatropic Rearrangement.** The thermal stereomutation of allylic sulfoxides was found to take another route, by rearrangement to a sulfenic ester which then can produce either stereoisomer (equation 3).[5,12] Even though the bond strengths for the benzylic ($PhCH_2$-X) and allylic ($CH_2$=$CHCH_2$-X) compounds are similar,[16,17] the stereomutation of allyl p-tolyl sulfoxide occurred at a much lower temperature range (50 – 70°C) than benyzl p-tolyl sulfoxide. The activation enthalpy (23 kcal/mol) was much lower than all other stereomutations (Table 1) and the activation entropy being negative (-5.0 e.u.) is consistent with forming a cyclic transition state. Several other allylic sulfoxides were investigated all giving activation ethalpies of 21 – 23 kcal/mol.[18]

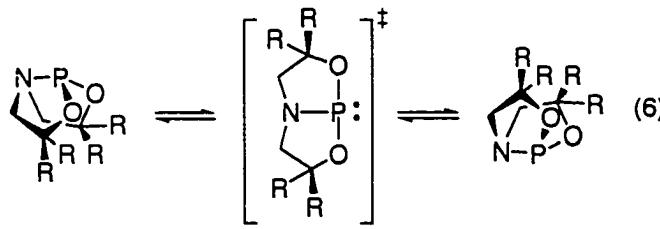
The sulfenate – sulfoxide thermal rearragement has recently been investigated for cinnamyl-4-nitrobenzenesulfenate (equation 5).[19] Convincing evidence has been presented against the concerted rearrangement, but in favor of a radical pair mechanism. The mechanism has been deduced from determination of a positive activation entropy (+ 6.4 eu), a secondary isotope effect ($k_H/k_D$ = 1.19), trapping an radical intermediate with TEMPO, and computation of the bond




(5)

dissociation energy C-O in agreement with experimental value (26 kcal/mol versus 28 kcal/mol, respectively).

**Edge Inversion.** Even though this mechanism has never been seriously proposed for sulfoxide inversions, it is interesting to visit this diversion to phosphorus inversion. Arduengo III and co-workers have experimentally and computationally determined that pnictogens can proceed either through pyramidal invervsion or edge inversion both producing the same inverted product.[20,21] When the inversion proceeds through the edge inversion mechanism the transition state forms a T-shape geometry (i.e. considering the lone pair a square planar structure is formed) instead of the planar transition state (i.e. considering the lone pair a trigonal bipyramidal structure is formed) formed from pyramidal inversion. It was found from computations that substitution at phosphorus by electronegative atoms promoted the edge inversion mechanism over the pyramidal inversion. i.e. $PF_3$ will undergo the edge inversion but $PH_3$ will proceed through the pyramidal inversion. The edge inversion barrier (53.8 kcal/mol) in $PF_3$ is much lower that the pyramidal inversion barrier (85.3 kcal/mol). The reverse effect is even more pronounced for $PH_3$, where the pyramidal inversion barrier is favored by 125 kcal/mol lower over the edge inversion barrier. For the molecule in equation 6, the experimental inversion barrier was determined to be 23.4 kcal/mol and calculated to be 28.1 kcal/mol at the MP2 level and with a double-zeta basis set,[22] thus giving supporting experimental evidence for the edge inversion mechanism.



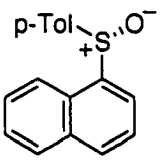

(6)

R, R = adamantyl (exp.)
R = H (calc.)

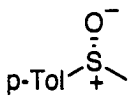
**Photochemical Stereomutation[2]**

In the literature there has been two mechanisms invoked to explain the photostereomutation of sulfoxides. Analogous to thermal stereomutation, pyramidal inversion and C-S bond cleavage mechanisms have been deduced corresponding to sulfoxide structure (equations 1 and 2).[23-26] In equation 2, the C-S bond is analogous to α-cleavage in carbonyl photochemistry and here after be referred to as α-cleavage.

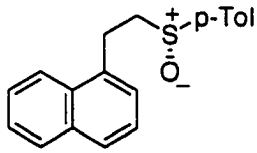
The first examples of photoinduced stereomutations of sulfoxides were investigated by Mislow, Hammond, and co-workers in 1960s.[27,28] Direct irradiation of degassed (-)-(S)-α-naphthyl p-tolyl sulfoxide (**1**) solution through a 285 nm cut-off filter yielded completely racemized sulfoxides in 70% yield plus some unidentified products. Intermolecular sensitization with naphthalene with (+)-(R)-methyl p-tolyl sulfoxide (**2**) produced only 40% recovered, 72% racemized sulfoxide. Irradiation of sulfoxide **3** provided completely racemized sulfoxide in 84% yield, via insulated intramolecular sensitization. It was found that a chromophore other than the sulfinyl moiety was necessary to achieve efficient racemization. Sulfoxide **4** did not undergo racemization, only decomposition. Sensitized photolysis with naphthalene of **2** and **3** was evalutated. Quenching of the excited states with piperylene (1,3-pentadiene) did not completely suppress racemization in either **2** (with direct irradiation) or **3**. From these experiments, it was suggested that both sulfoxides racemized out both of the singlet and triplet manifolds.



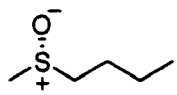

**1**




**2**



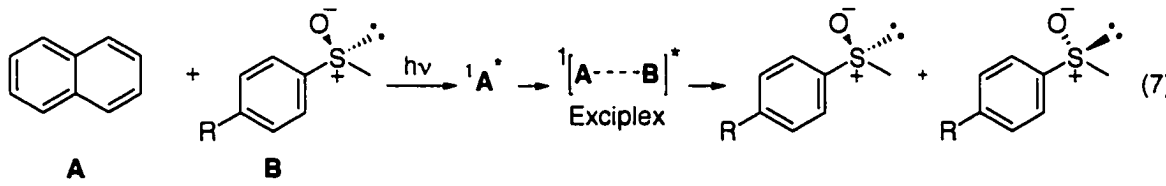

**3**




**4**

In a latter publication Cooke and Hammond further studied the naphthalene-sensitized photoracemization of para-substituted sulfoxides.[29,30] Since both the singlet and the triplet energies of naphthalene (92 kcal/mol and 61 kcal/mol, respectively)[31] were lower than the respective state energies of sulfoxides (approximately 113 kcal/mol (singlet state) and 79 kcal/mol (triplet state)), exciplex formation between naphthalene and sulfoxide was suggested (equation 7). From

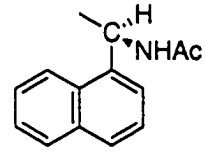
sensitization experiments, the authors concluded that the singlet excited state of naphthalene was involved in the exciplex formation and not the triplet excited state. The quenching rate constants were evaluated for various para-substituted electron donating and withdrawing substituents on the benzene ring and no dependence was observed. No direct spectroscopic evidence was shown for exciplex formation.




**A** **B** (7)

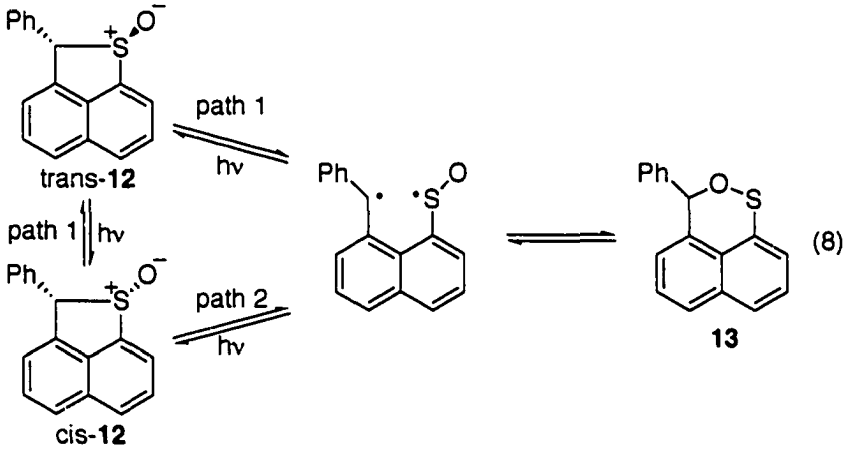
Charlesworth et al. have shown support for exciplex formation by determining the quenching rate constants for many substituted aryl sulfoxides.[32] The aromatic sulfoxides were found to quench aromatic sensitizers whose singlet energies are much lower than their own. The overall rate constant profile for the series of sulfoxides and sensitizers that were studied is consistent with electron transfer and/or exciplex formation for quenching. From cyclic voltammetry, the authors determined that the direction of charge transfer is from sensitizer to sulfoxide.

Another example of sensitized pyramidal inversion was carried out with the sensitization of racemic (±)-methyl p-tolyl sulfoxide with irradiated ((**+**)-(**R**)-**5**).[33] The reaction produced a slight enantiomeric excess of (+)-(R)-methyl p-tolyl sulfoxide. The reverse reaction was run where racemic sensitizer **5** was employed with (+)-(R)-methyl p-tolyl sulfoxide in optical excess. The results produced a racemic mixture of sulfoxides, thus validating the effect of using a chiral sensitizer for the possibility of optical resolution.

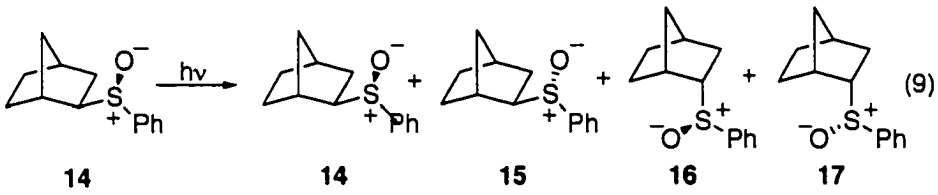



**(+)-(R)-5**

In 1970, Schultz and Schlessinger investigated the role of a sulfenate ester intermediate in sulfoxide photoracemization using racemic **12**.[34] Although not required from their data, the authors suggested that the photoracemization proceeded mostly through pyramidal inversion (path 1, equation 8) in the excited state with little or no barrier before internal conversion to the ground state. Sensitized irradiation of trans- and cis-**12** at 366 nm produced a 1:4 photostationary state between the two sulfoxides, respectively. The quantum yields were measured to be different for the trans- and cis-**12**, 0.70 and 0.18, respectively. This result must indicate that some, if not all, of the photo-inversion must be coming from radical pair recombination after α-cleavage, since a much higher quantum yield of the more stable trans-**12** is realized (path 2, equation 8). After a long duration of sensitized photolysis, sultene **13** was afforded albeit in small amounts (2% yield) via α-cleavage.



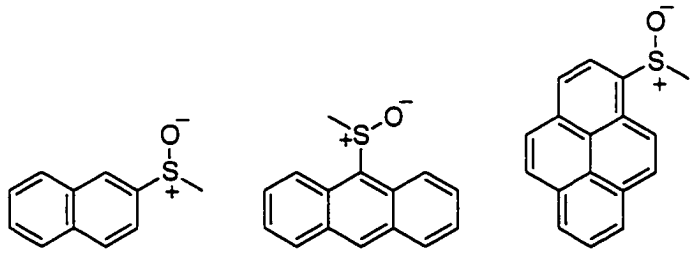

Kropp and colleagues provided clear evidence for a radical mechanism during the photolysis of 2-norbornyl sulfoxides.[35] Photostereomutation was observed upon irradiation of (2R*, $R^*_S$)-2-norbornyl phenyl sulfoxide **14**, producing a 0.7:1 photo-equilibrium of **14** and **15** (equation 8). Sulfoxides **16** and **17** were also present in the reaction mixture. These products being present strongly indicate C-S scission followed by radical recombination producing epimers of **14** and **15**. The product majority favoring **14** and **15** could be due to diastereomeric preference or direct pyrimidal inversion through a photostationary state.



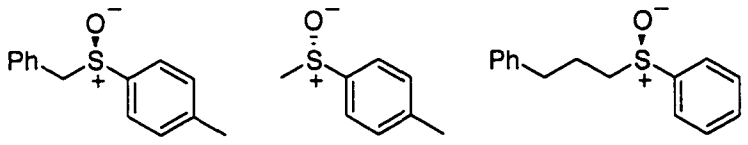

**14** **14** **15** **16** **17**

Recently, Lee and Jenks investigated the photoracemization of aryl methyl sulfoxides and produced data consistent with pyramidal inversion.[26] With the assistance of an HPLC chiral-phase column, quantum yields of inversion were determined for sulfoxides **6**, **7** and **8**. The quantum yields for inversion for all of sulfoxides were high (~0.2) and quantum yields for other chemical reactions were low (< 0.01). The authors concluded that racemization was closely related to the nonradiative decay of a singlet state. This mechanism was validated by the lack of racemization upon triplet sensitization and the lack of quenching of racemization with dienes. From an Arrhenius study of the racemization of 1-methanesulfinylpyrene, only a modest activation energy of a few kcal/mol was estimated. Results on the photoinversion reaction of various sized diaryl sulfoxides[25] are supported by the conclusion of Lee and Jenks.

Guo and Jenks investigated the α-cleavage and stereomutation mechanisms during the photolyses of alkyl aryl sulfoxides.[36] The authors determined quantum yields loss of optical activity ($\Phi_{rot}$) and loss of starting material ($\Phi_{loss}$) for chiral sulfoxides **9**, **10**, and **11**. The $\Phi_{loss}$ is much higher and the $\Phi_{rot}$ is much lower for sulfoxide **9** than for **10** and **11** (Table 3), thus suggesting α-cleavage for **9** (although some inversion could occur through direct pyramidal inversion) and pyramidal inversion for **10** and **11**. Although the results of Guo and Jenks support pyramidal inversion, their results cannot definitively rule out the α-cleavage mechanism being partially or even fully responsible.



**6** **7** **8**



(+)-(R)-**9** (-)-(S)-**10** (+)-(R)-**11**

**Table 3**. Quantum Yields for Loss of Starting Materials and Optical Activity[36]

| | (+)-(R)-**9** | (-)-(S)-**10** | (+)-(R)-**11** |
|---|---|---|---|
| Solvent, λ (nm) | $\Phi_{rot}$ ($\Phi_{loss}$) | $\Phi_{rot}$ ($\Phi_{loss}$) | $\Phi_{rot}$ ($\Phi_{loss}$) |
| i-PrOH, 267 | 0.44 (0.30) | 0.90 (0.036) | 0.85 (0.037) |
| t-BuOH, 267 | 0.42 (0.21) | 0.83 (0.038) | 0.81 (0.036) |

Several other studies found similar results that could be explained by both pyramidal inversion and/or α-cleavage in the photoracemization of various sulfoxides.[37-40] In the studies above, α-cleavage is definitely present in some amount, due to formation of decomposition products.

**Present Investigation**

As has been presented in the introduction, there have been numerous examples on photo-racemization of chiral sulfoxides, but obviously there is controversy by which mechanism (α-cleavage or inversion) does the racemization occur. By gaining insight into the energetics of excited state potentials computationally, we hope to help alleviate some of the controversy on the mechanism of photoracemization of sulfoxides and provide structural information of sulfoxides on the excited state potential. Since a photostationary state has been proposed for the photoinversion of sulfoxides,[34,35] this system may be reminiscent of excited state olefin isomerization.[41]

Even though $H_2SO$ and $(CH_3)_2SO$ (DMSO) are not chiral sulfoxides, they were chosen as model sulfoxides to provide a starting point for a relatively complicated study. Experimentally the existence of $H_2SO$ is not known, but its small size makes it amendable for this study to save computer time. Gregory and Jenks[42] have found carbon substitution at sulfur changes the energetics, therefore DMSO is used to observe the effect of carbon substitution on photo-inversion. Since it is known that to correctly get the energetics of sulfoxides correct, a large basis set must be used (see Chapter 1). It was imperative to start with these smaller symmetric sulfoxides. This allowed us to gain a handle

on the excited state potentials (using symmetry) without sacrificing large amounts of computation time and provide a basis to investigate larger molecules such as methyl phenyl sulfoxide.

## Computational Methods

ROHF methods are used with Boys localization protocol[43] to gain good starting orbitals for the active space of the multiconfiguration self-consistent field (MCSCF) calculations.[44] MCSCF methods are employed to compute the excited states. A full optimized reaction space (FORS) is used to allow full mixing of active electrons with all active orbitals.[45] This method is also know as complete active space SCF (CASSCF).[45] Electron correlation outside the active orbital set is recovered on the MCSCF wavefunction by using the multiconfiguration quasidegenerate perturbation theory (MCQDPT).[46,47] MCQDPT allowed achievement of realistic excitation energies, since it is known that MCSCF does not compute energetics accurately.[44] For the MCSCF and MCQDPT calculations, full valence active space is chosen for $H_2SO$ that is 14 electrons in ten orbitals [14,10]. In DMSO, the analogous active space leaves out only the C-H bonds, since they do not participate in the racemization. The basis sets chosen for $H_2SO$ and DMSO was 6-311+G(3df,2p) and 6-311+G(3df), respectively. The extra polarization functions on hydrogens were found not to effect the relative energies of DMSO in test geometries. Ground state optimizations were completed using both MP2 and MCSCF levels of theory.

The convergence of the excited state MCSCF wavefunctions was achieved by first computing the triplet MCSCF wavefunction and using those orbitals as starting orbitals for the excited singlet states. Then it was found that the singlet A' states MCSCF wavefunction converged only with second order SCF (SOSCF) method.[48] The full Newton-Raphson orbital improvement (FULLNR) method was used to obtain the singlet A" states, both triplet A' and A" states, and all $C_{2v}$ exicited states.[49]

All computations were carried out with the GAMESS suite of programs.[50] All molecules and orbitals were viewed with MacMolPlt graphical interface for GAMESS.[51] All least linear motion paths (LLMP) were constructed using internal coordinates (Z-matrices) using MacMolPlt.

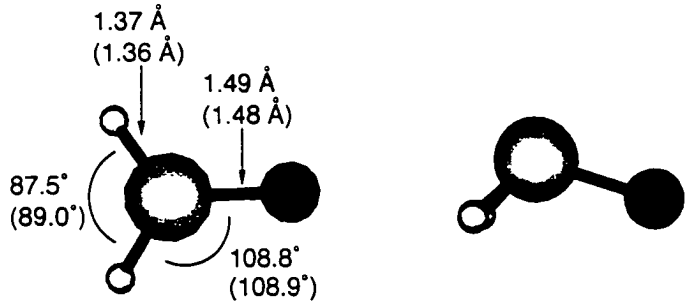
# Results

## Thermal Inversion

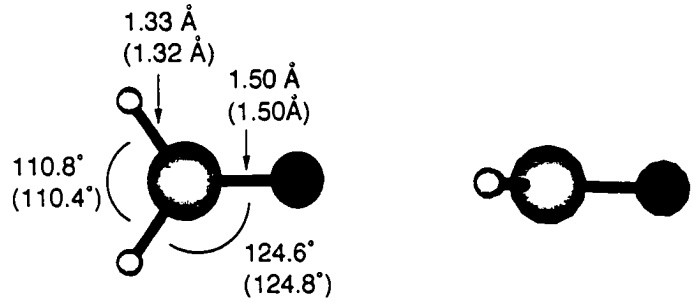
**Ground State Geometries.** For both $H_2SO$ and DMSO, the ground state thermal inversion potential was assumed to proceed from the pyramidal form with $C_s$ symmetry (equilibrium structure) through a planar transition state ($C_{2v}$ symmetry). These structures are shown for $H_2SO$ and DMSO in Figures 2 and 3, respectively.

The structures for $H_2SO$ were optimized at both the MP2/6-311+G(3df,2p) and CASSCF[14,10]/6-311+G(3df,2p) levels of theory and basis sets. The pyramidal structure was calculated to have as expected much tighter HSH and HSO bond angles than the in the planer transition state (Figure 2). Consistent with previous calculations on $H_2SO$,[13] the S-O bond is lengthened in the planar transition state. The computed planar transition structure has one imaginary frequency that corresponds to the collapse to the pyramidal structure. Both levels of theory do an adequate job in producing very similar structures.

The trends computed for DMSO are similar to those calculated for $H_2SO$. The geometries for DMSO were optimized at MP2/6-311+G(3df), at MP2/6-311+G(3df,2p), and at CASSCF[14,10]/6-311+G(3df,2p). All three levels of theory produce similar structures and are all in reasonable agreement with the gas phase geometry obtained from microwave spectroscopy for the $C_s$ equilibrium geometry (Figure 3).[52] The CASSCF[14,10]/6-311+G(3df) level of theory seems to give a structure that was slightly better in agreement with the experimental structure (i.e. C-S bond length (1.80 Å (calc.) versus 1.808 Å (exp.)). There is no effect on the C-S or S-O bonds from removing the p-polarization functions from the hydorgens as observed MP2 optimized structures at the different basis sets in Figure 3.




a) $C_s$ $H_2SO$ (**18**)




b) $C_{2v}$ $H_2SO$ (**19**)

**Figure 2.** $H_2SO$ optimized structures: a) equilibrium geometry ($C_s$ symmetry) and b) thermal transition state ($C_{2v}$ symmetry). The structures on the right are depicting side view showing a) pyramidal structure and b) planar structure. Bond lengths depicted as calculated at MP2/6-311+G(3df,2p) and in parentheses at CASSCF[14,10]/6-311+G(3df,2p).

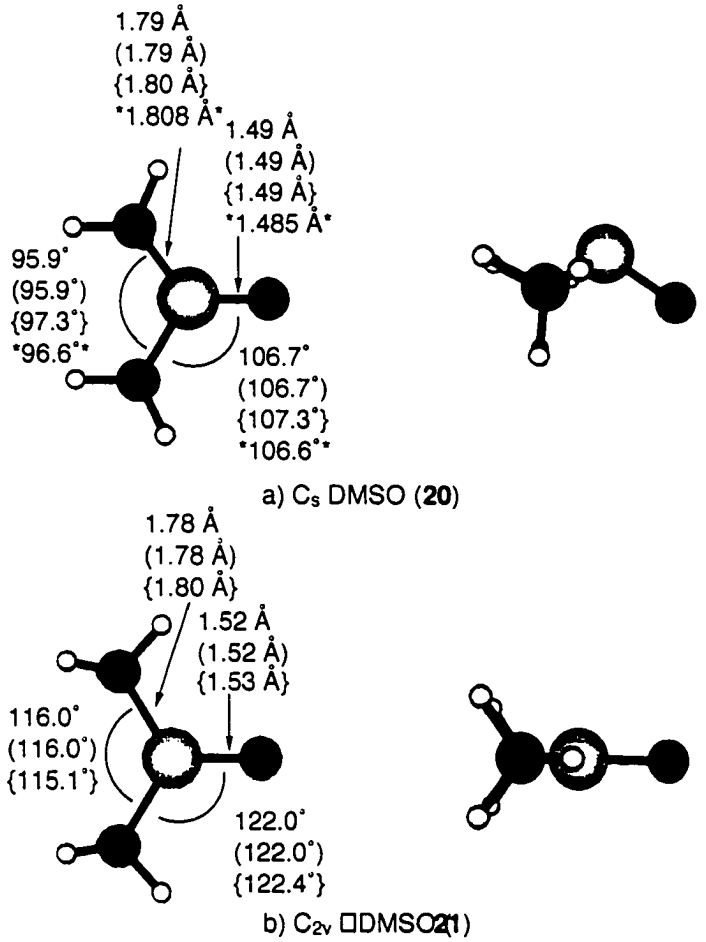



**Figure 3**. DMSO optimized structures: a) equilibrium geometry ($C_s$ symmetry) and b) thermal transition state ($C_{2v}$ symmetry). The structures on the right are depicting a side view showing a) pyramidal structure and b) planar structure. Bond lengths depicted as calculated at MP2/6-311+G(3df), in parentheses, at MP2/6-311+G(3df,2p), in braces, at CASSCF[14,10]/6-311+G(3df,2p), and in stars, gas phase experiment.[52]

**Ground State Inversion Barriers**. The calculated barriers to inversion for $H_2SO$ and DMSO are shown in Table 4. For $H_2SO$, the inversion barrier calculated at the MP2/6-311+G(3df,2p) level of theory and basis set was found to be 39 kcal/mol (unscaled zero-point energy included), in good agreement with the MP2/6-311+G(2d,p) calculated values found by Fueno and colleagues.[13] However, the CASSCF level the barrier was considerably higher (58 kcal/mol), until perturbation

**Table 4.** Computed Ground State Inversion Barriers

| | $H_2SO$[a] (kcal/mol) | DMSO[a] (kcal/mol) |
|---|---|---|
| MP2/6-311+G(3df,2p) | 39.1 | 51.0 |
| CASSCF/6-311+G(3df,2p)[b] | 58.3 | |
| MCQDPT/6-311+G(3df,2p)[b,c] | 31.9 | |
| MP2/6-311+G(3df) | | 50.9 |
| CASSCF/6-311+G(3df)[b] | | 67.6 |
| MCQDPT/6-311+G(3df)[b,d] | | 41.5 |
| CASSCF/6-311+G(3df)[b,e] | | 67.7 |
| MCQDPT/6-311+G(3df)[b,e] | | 43.6 |
| Experimental[f] | | 37.4 |

[a]All values are corrected with ZPE from MP2/6-311+G(3df,2p) hessians. [b]The active space is [14,10]. [c]Single point energy on the CASSCF/6-311+G(3df,2p) optimized geometry. [d]Single point energy on the CASSCF/6-311+G(3df) optimized geometry. [e]Single point energy on the MP2/6-311+G(3df,2p) optimized geometry. Value for methyl p-tolyl sulfoxide.[6]

theory was applied for energy correction. The inversion barrier was reduced to 32 kcal/mol at MCQDPT/6-311+G(3df,2p)//CASSCF[14,10]/6-311+G(3df,2p) as shown in Table 4.

For DMSO, the effect of the basis set was evaluated for the inversion process. Comparison of MP2/6-311+G(3df,2p) versus MP2/6-311+G(3df) found the extra polarization functions on hydrogens to have almost no effect on the relative energies (Table 4). A similar trend that was observed with $H_2SO$, in going from the CASSCF to the MCQDPT level of theory, was also observed with DMSO. At the MCQDPT/6-311+G(3df)//CASSCF/6-311+G(3df) and MCQDPT/6-311+G(3df,2p)//MP2/6-311+G(3df,2p) levels of theory and basis sets both give inversion energetics consistent with values determined experimentally for related asymmetric sulfoxides[6] (see Tables 1 and 4).

## Excited State Results

**$H_2SO$ Vertical Excitation.** In following our hypothesis from Figure 1, we felt that if the vertical excited states of the ground state **18** correlated with the vertical excited states of transition state **19** for $H_2SO$, the vertical excited states of **19** might be lower in energy than the vertical excited states of **18**. Although the vertical excited states of **19** could never be accessed physically, this gave us a starting point. Indeed, it was found that the vertical A' states of ground state **18** were higher in

energy and correlated to the vertical states of **19** (Figures 4 and 5). However, the A" state of **18** lies lower in energy that $B_2$ state of **19**. The correlation for the A' to $B_1$ states can be easily made in Figure 5, whereas A" state does not seem to directly correlate. As shown below in a subsequent section, an A" state does correlate to the $B_2$ state. Both the triplet and singlet natural occupied orbitals are similar.

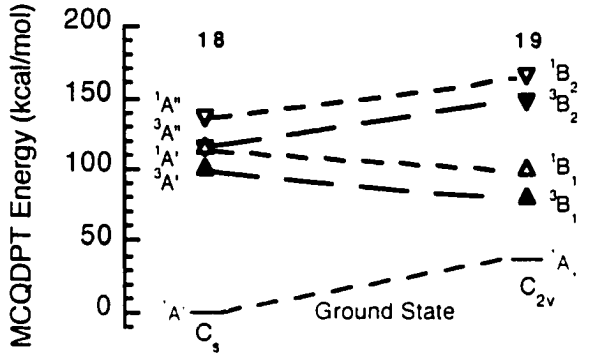



**Figure 4**. Vertical energies of **18** and **19**

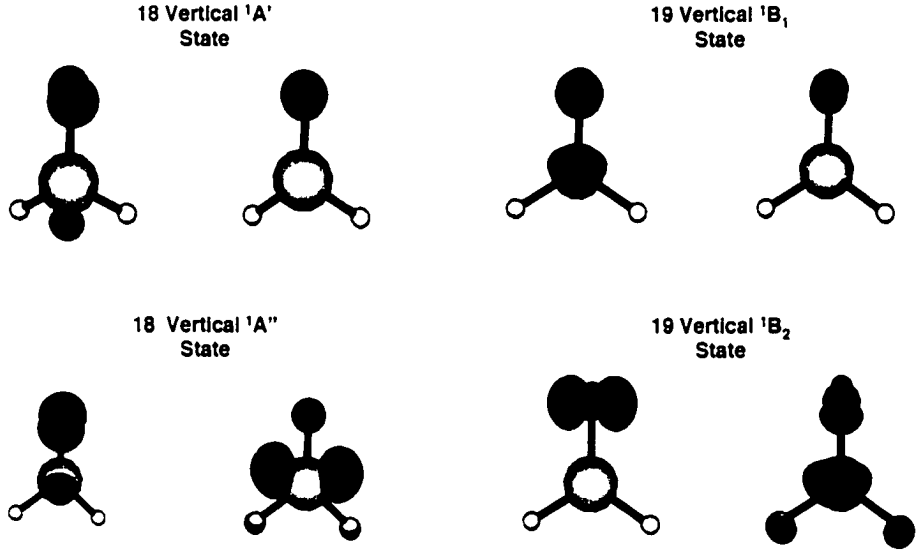



**Figure 5**. Singly occupied natural orbitals for the vertical states of **18** and **19**.

As shown in Figure 4, the first vertical excited state ($^3A'$) lies at 101 kcal/mol above the ground state at MCQDPT/6-311+G(3df,2p)//CASSCF[14,10]/6-311+G(3df,2p). This would correspond to an absorption $\lambda_{max}$ of 283 nm. The lowest lying singlet state ($^1A'$) is 116 kcal/mol above the $C_s$ equilibrium geometry ($\lambda_{max}$ = 246 nm). These two states correlate with the vertical $B_1$ states of the $C_{2v}$ geometry. The $^3B_1$ and $^1B_1$ vertical states are 44 and 64 kcal/mol above the $C_{2v}$ thermal transition state, respectively. $^3A''$ and $^1A''$ prime states exist above the A' states. Both of these states correlate to the $B_2$ states of the $C_{2v}$ thermal transition state geometry, lying much higher in energy than the $B_1$ states.

**Relaxed Excited State Geometries of $H_2SO$.** Once it was realized that correlating states in $C_s$ and $C_{2v}$ symmetry could be found and that, when at the ground state geometries, the $C_{2v}$ states had lower energies (by 19 and 14 kcal/mol in triplet and singlet manifolds, respectively). It obviously became attractive to try to find optimized geometries for these states. Relaxed excited state geometries for the four singlet excited states ($^1A'$, $^1A''$, $^1B_1$, $^1B_2$) and the four triplet states ($^3A'$, $^3A''$, $^3B_1$, $^3B_2$) were computed (Figures 6 and 7, respectively). All of these structures were optimized at the CASSCF/6-311+G(3df,2p) level of theory and basis set and found to be stationary points on the excited surface. Hessians (second derivatives) were attempted to classify these states as minima on the excited state potential but all attempts at collecting the hessians failed. While calculating the hessian, it is necessary to remove the symmetry constraints in which then both the excited state and the ground state become the same symmetry. Therefore, the hessian ultimately converges on the wrong state, if it converges at all.

Structures **18** $^1$**A'** and **18** $^1$**A"** of $C_s$ symmetry are similar (Figure 6). They both have S-O bond lengthening, decreased HSO angles, and increased HSH angles when compared to ground state **18** in Figure 2. The major differences between the two excited structures are the amount of S-O bond lengthening in **18** $^1$**A"** and the increased HSH bond angle in **18** $^1$**A'**. The energetics are presented below.

The $C_{2v}$ structures **19** $^1\mathbf{B_1}$ and **19** $^1\mathbf{B_2}$ are dramatically different from the ground state analog **19** in Figure 2. There is S-H bond deformation comparing **19** to both of the $C_{2v}$ excited state

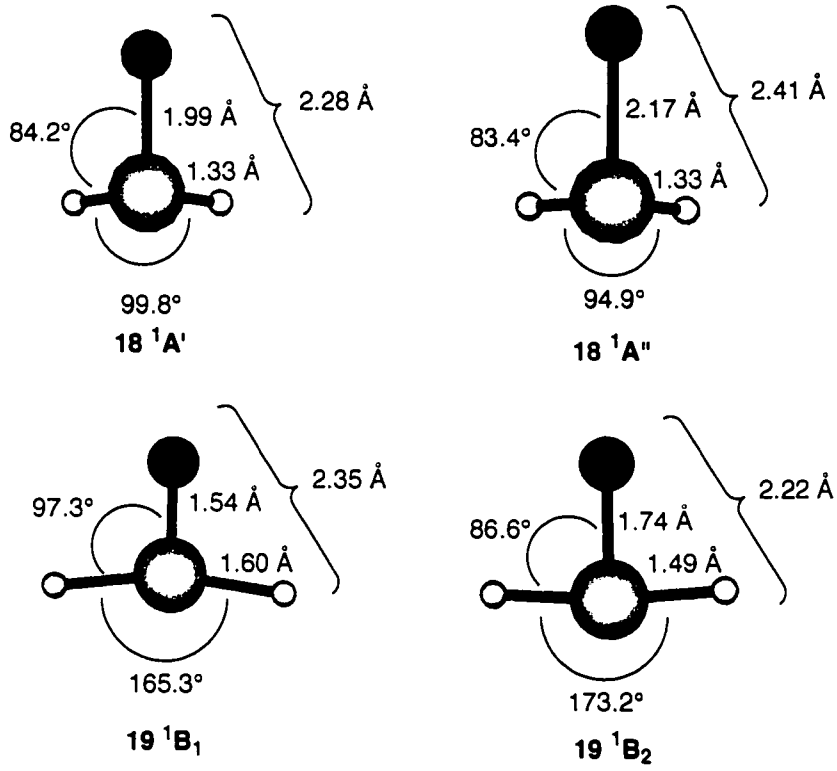



**Figure 6.** Singlet state relaxed geometries for $H_2SO$ calculated at CASSCF[14,10]/6-311+G(3df,2p). Braces are showing H-O bond distances.

structures. Although, being very different from the ground state structure, **19** $^1$**B**$_1$ and **19** $^1$**B**$_2$ are somewhat similar in geometry. Both structures are nearly T-shaped, reminiscent of the geometry in $ClF_3$, sulfuranyl radicals,[53] and pnictogens.[22] The major differences between **19** $^1$**B**$_1$ and **19** $^1$**B**$_2$ are the S-H and S-O bond lengthening, respectively.

The optimization of the triplet structures only produced three bound states (Figure 7). Structure **18** $^3$**A'** was observed as a stationary point that is obviously not a bound structure with the O atom being 4 Å away from sulfur of $H_2S$. Several other beginning structures were attempted and no $^3$**A'** bound was observed. The $C_{2v}$ relaxed triplet structures (**19** $^3$**B**$_1$ and $^3$**B**$_2$) are very similar to the singlet geometries (**19** $^1$**B**$_1$ and $^1$**B**$_2$). The **18** $^3$**A"** geometry is somewhat different from the **18** $^1$**A"**. The S-O and H-S bonds are nearly equal in length and the HSH and HSO bond angles are very similar to the ground state structure **18**.

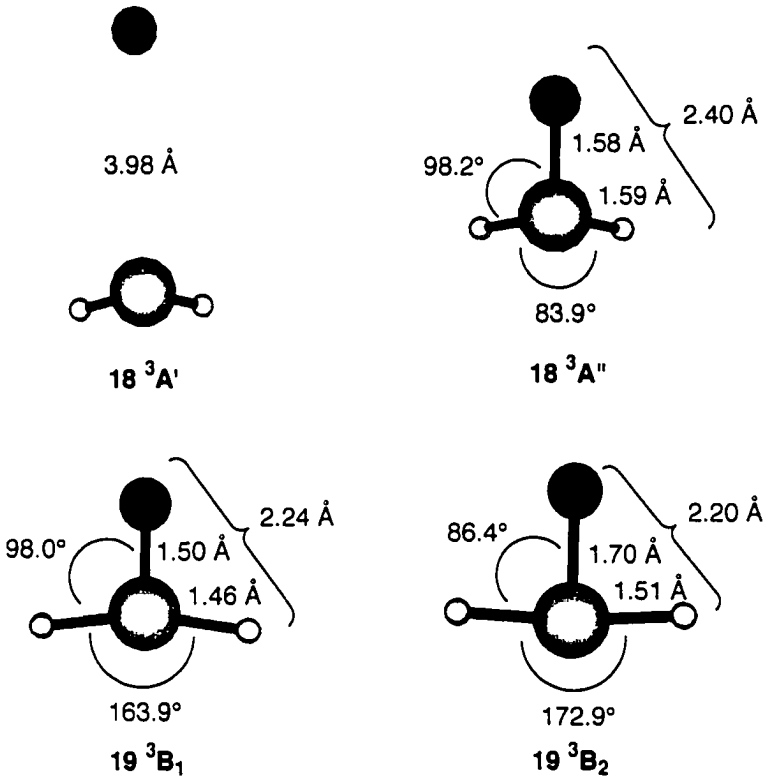



**Figure 7**. Triplet state relaxed geometries for $H_2SO$ calculated at CASSCF[14,10]/6-311+G(3df,2p) Braces are showing H-O bond distances.

Two other $C_s$ $^1$A" states were found as stationary points (Figure 8). Structures **18 $^1$A"a** and **18 $^1$A"b** are quite different in geometry from each other. The excited state **18 $^1$A"b** is in close resemblance to **19 $^1$B$_2$** (Figure 6). It is much flatter than the other $C_s$ structures located. It is also notable that the H-O distance is much closer (2.1Å) than in any of the other stationary structures. Structure **18 $^1$A"a** is very similar to the triplet molecule **18 $^3$A"** except for a much shorter S-H bond in **18 $^1$A"a**. The singly occupied natural orbitals for these relaxed geometries are shown Figure 9.

Now a correlation can be drawn from the orbitals of relaxed **18 $^1$A"** to vertical **19 $^1$B$_2$** (Figure 5). There is a resemblance of the orbitals of vertical **18 $^1$A"** to relaxed **18 $^1$A"a**. As shown below, the A" path has many low lying states that end in forbidden crossings.

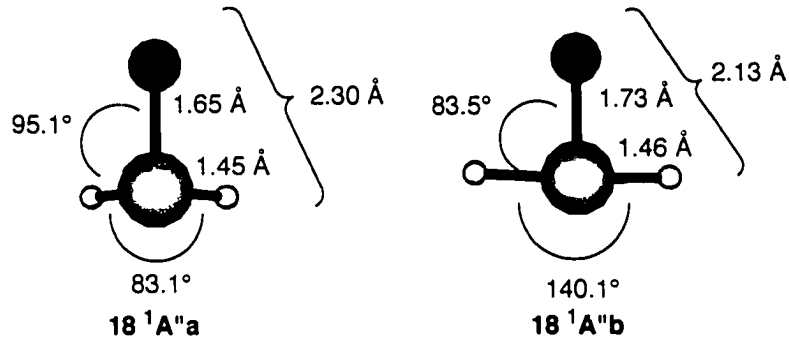



**Figure 8**. Two additional singlet relaxed structures

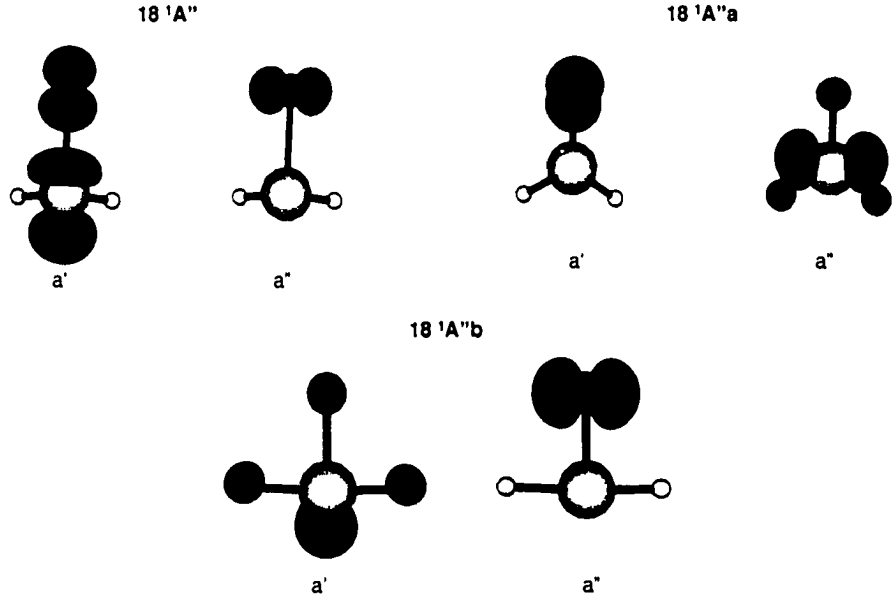



**Figure 9**. Singly natural occupied orbitals for the ¹A" relaxed geometries

**Relaxed Geometry Energetics for $H_2SO$.** The relaxed energetics for $H_2SO$ are depicted at the CASSCF[14,10]/6-311+G(3df,2p) and MCQDPT/6-311+G(3df,2p)//CASSCF[14,10]/6-311+G(3df,2p) levels of theory and basis set in Figures 10. Examination of the figure show that MCQDPT lowers the energy of all the excited states, compared to CASSCF. It should also be noted that the **18** $^1$**A"** and **18** $^1$**A'** are switched, and **18** $^1$**A"** is lower by 33 kcal/mol than **18** $^1$**A'** at the MCQDPT level of theory.

Assuming reliable energetics with MCQDPT, structure **18** $^1$**A"** is 84 kcal/mol and structure **18** $^1$**A'** is 88 kcal/mol above the ground state **18**. These two relaxed geometries, **18** $^1$**A"** and **18** $^1$**A'**, correlate with relaxed geometries of **19** $^1\mathbf{B_2}$ and **19** $^1\mathbf{B_1}$, respectively. Structure **19** $^1\mathbf{B_2}$ is 14 kcal/mol higher in energy than **18** $^1$**A"**, where as **19** $^1\mathbf{B_1}$ is 27 kcal/mol lower in energy than **18** $^1$**A'** (Figure 10).

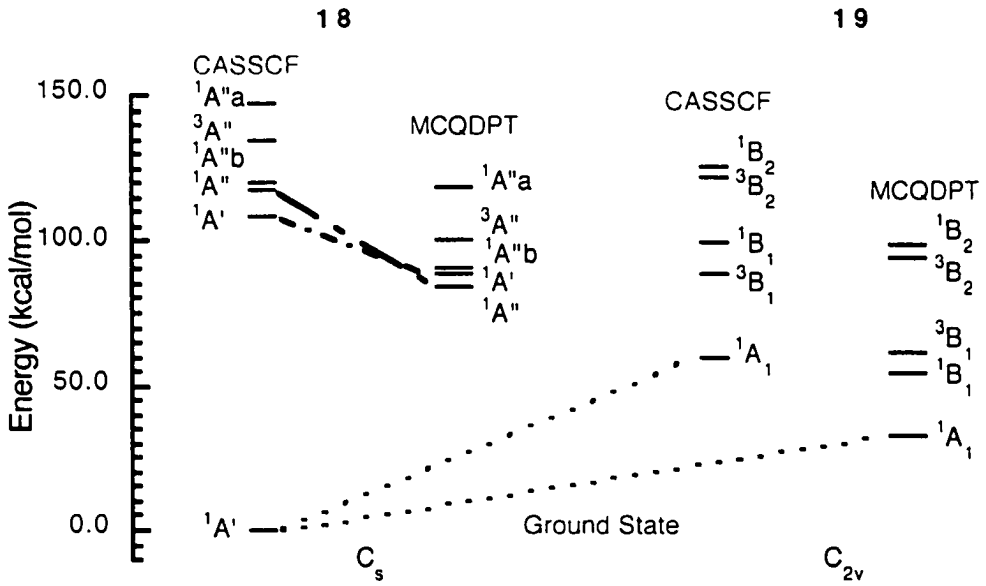



**Figure 10.** Energetics of relaxed geometries for $H_2SO$. States are labeled according Figures 5, 6, and 7 (i.e. **18** $^1$**A"a** = $^1$A"a).

**Least Linear Motion Pathways (LLMP) for $H_2SO$.** It was hoped that once the vertical excited state for the ground state $C_s$ geometry was correlated to the lower energy $C_{2v}$ excited state, the states could be connected via an intrinsic reaction coordinate (IRC) method. All attempts to get the IRC to run failed because it either would not converge on the right state or jump off the first point.

Therefore, the best compromised to connect the geometries was to use least linear motion pathways. The LLMP should provide an upper bound on the barrier, since it moves atoms in the shortest distance between geometries. The sections below LLMPs are constructed for the vertical geometry (**18**) to vertical geometry (**19**), relaxed excited (**18** $^1$**A'** and **18** $^1$**A"**) geometry to relaxed excited geometry (**19** $^1\mathbf{B_1}$ and **19** $^1\mathbf{B_2}$), and vertical geometry (**18**) to relaxed excited geometries (**19** $^1\mathbf{B_1}$, **19** $^1\mathbf{B_2}$, **19** $^3\mathbf{B_1}$, and **19** $^3\mathbf{B_2}$). The most realistic LLMP is the vertical geometry to relaxed geometry, since this path is the photochemical event.

**Vertical geometry to vertical geometry LLMP for H2SO.** A least linear motion path (LLMP) was constructed connecting the ground state $C_s$ equilibrium geometry to the $C_{2v}$ thermal transition state geometry for $H_2SO$ (Figure 10). Ten geometries were chosen between the $C_s$ and $C_{2v}$ structures. Utilizing the functionality of the CASSCF calculation to select the spin multiplicity and excited state symmetry, one arrives at the vertical excitation energy. Once the CASSCF method produces the vertical state, perturbation theory (MCQDPT) can be applied on top the CASSCF wavefunction to achieve more realistic vertical excitation energies. From following the vertical excitation energies from the $C_s$ structure to the $C_{2v}$ structure, a correlation diagram of the excited states can be drawn. Figure 11 shows the vertical excitation for $H_2SO$ for the four lowest lying states.

Close examination of the orbitals of the LLMP geometries in Figure 11, reveals the A' orbitals correlate directly to those of the $B_1$ state. However, the identities of the singly occupied orbitals along the A" path orbital change between points 3 and 4. The orbital change is depicted in Figure 12. Points 1 – 3 on the A" resemble **18 A"x** and at point 4 the orbitals switch and resemble **18 A"y**. This can be regarded to as a forbidden crossing. After point 4 the orbitals now correlate with the orbitals of state **19** $\mathbf{B_2}$ (Figure 5). The triplet and the singlet orbitals undergo this same change.

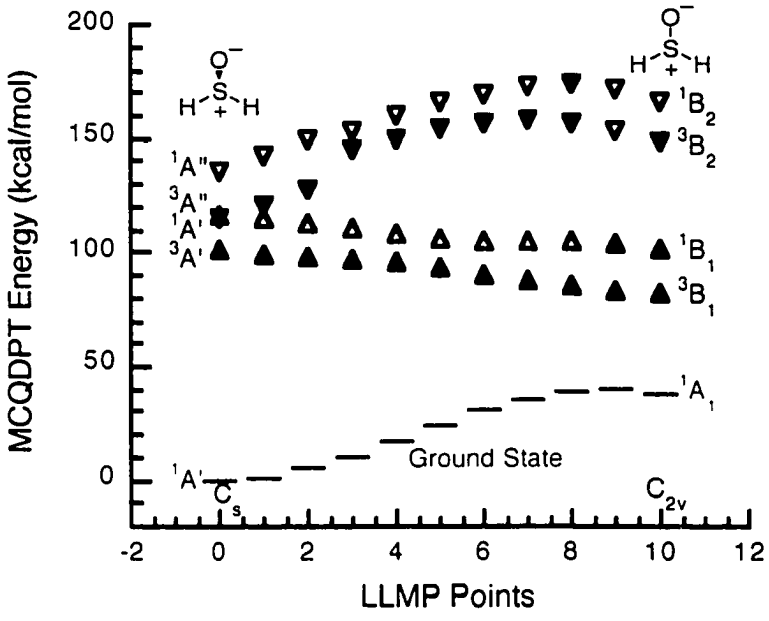



**Figure 11**. Correlation of the first four vertical excitation states for both single and triplet spin states with the ground state LLMP between the $C_s$ structure and $C_{2v}$ structure for $H_2SO$.

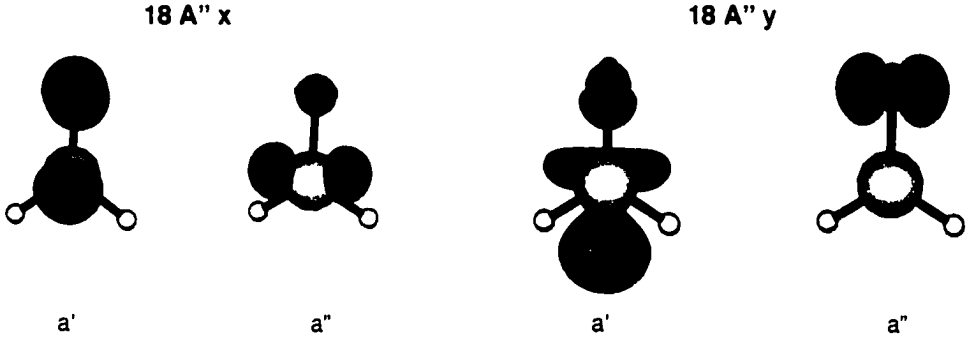



**Figure 12**. Singly occupied natural orbitals that change at points 3 and 4 in Figure 11.

**Relaxed geometry to relaxed geometry LLMP for $H_2SO$.** Since **18** $^1$**A'** correlated with **19** $^1B_1$, a LLMP was constructed with 9 nine geometries in between starting and ending structures. In addition a LLMP was constructed between **18** $^1$**A"**and **19** $^1B_2$. The energetics are presented in Figure 13 at the MCQDPT/6-311+G(3df,2p)//CASSCF[14,10]/6-311+G(3df,2p) level of theory and basis set. A barrier of 9 kcal/mol can be observed in going from **18** $^1$**A'** to **19** $^1B_1$ and a much larger, 24 kcal/mol barrier is produced in going from **18** $^1$**A"**and **19** $^1B_2$. Many different convergence criterion were tried on the CASSCF wavefunction, but all failed for points 7, 8, and 9 for the $^1$A' path. It should be noted that the first excited state and the ground state are of the same symmetry.

On examination of the A" path in Figure 13, at points 3 and 4 the orbitals again switch. This time the orbitals start with the configuration of **18 A"y** (Figure 12) and then change into a configuration resembling the orbitals of **18** $^1$**A"b** (Figure 9). Finally, one last orbital change between points 9 and 10 in Figure 13, orbitals of **18** $^1$**A"b** become those resembling vertical **19** $B_2$ in Figure 5.

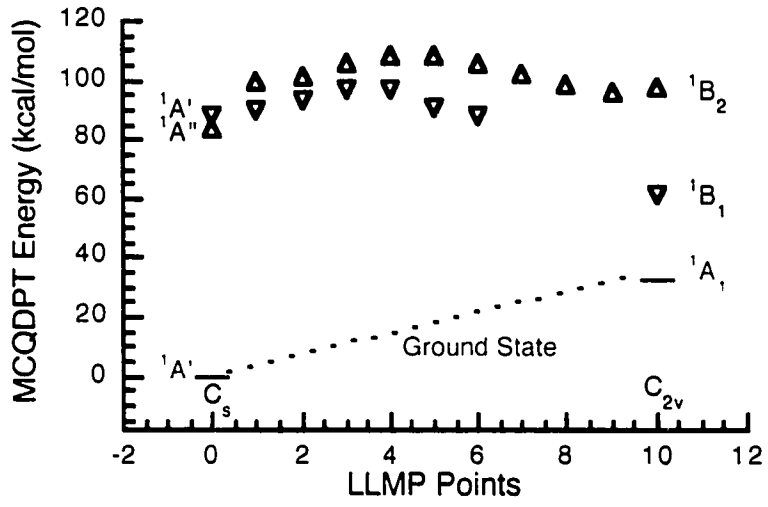



**Figure 13.** Relaxed to relaxed LLMP for $H_2SO$.

**Vertical geometry to relaxed geometry for $H_2SO$.** A LLMP was constructed from **18** to each of the following geometries **19** $^1B_1$, **19** $^1B_2$, **19** $^3B_1$, and **19** $^3B_2$. This should be the most physically related path, since when a molecule absorbs light, it is promoted into an excited state with

ground state geometry and then can relax to a different geometry if energetically accessible. Figures 14 and 15 show the energetics for the singlet and triplet pathways, respectively.

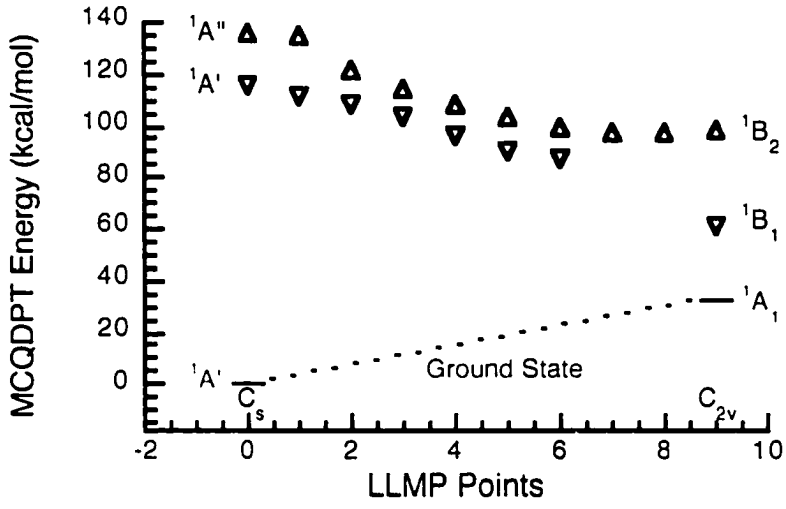



**Figure 14.** LLMP for $H_2SO$ singlet vertical to relaxed pathway.

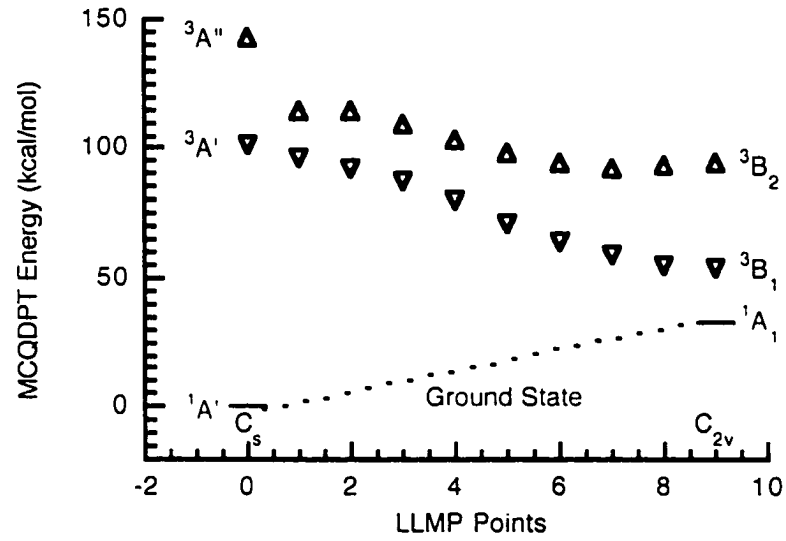



**Figure 15.** LLMP for $H_2SO$ triplet vertical to relaxed pathways.

In Figures 14 and 15, the LLMPs show that after the vertical excitation of **18** to both the singlet (Figure 14) and triplet (Figure 15) A' states, there is a steady decline in energy to their respective spin relaxed structures, **19** $^1B_1$ and **19** $^3B_1$, on the $C_{2v}$ surface. The vertical excitation at MCQDPT/6-311+G(3df,2p)//CASSCF[14,10]/6-311+G(3df,2p) level of theory and basis set from **18** down to **19** $^1B_1$ results in a 55 kcal/mol loss of energy. Convergence of the CASSCF wavefunction was again a problem the points closer to **19** $^1B_1$ on the $^1A'$ potential. The triplet surface shows a similar loss of energy (47 kcal/mol) from vertical excited **18** to relaxed **19** $^3B_1$.

Both the singlet and triplet A" states are not so well behaved. From vertical **18** on the $^1A"$ path, at first glance looks like a smooth decline in energy (38 kcal/mol) down to relaxed **19** $^1B_2$. With closer observation of Figure 14, between point 2 and 3 a forbidden crossing on the $^1A"$ surface is occurring on the LLMP, as there is another low lying $^1A"$ state (see Figure 12 for orbital change). A similar orbital change is observed between points 2 and 3 on the triplet A" surface (Figure 15). This led to calculation via state averaging for each the 3 lowest lying $^1A'$ states and the 2 lowest lying $^1A"$ states on the LLMPs between vertically excited **18** and **19** $^1B_1$, **18** and **19** $^1B_2$ (Figure 16).

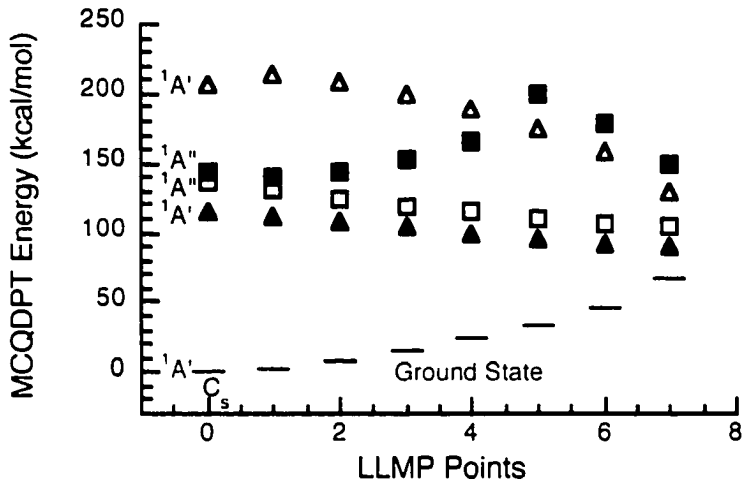



**Figure 16**. State averaged LLMP for $H_2SO$

Figure 16 depicting the LLMP the state averaged results from vertically excited **18** to **19** $^1B_1$, presents that the $^1A'$ states are all far apart from each other and are well behaved. However, on the $^1A"$ surface the first 2 points are very close in energy (<10 kcal/mol) apart. Those are the two states

that must be crossing in the pure $^1A''$ state analysis. In addition in Figure 16 at point 5 on the highest energy A" surface, there looks to be another even higher lying A" state close in energy although this has not been confirmed by averaging in the third higher A" state. State averaging was not performed on the triplet surfaces.

**DMSO Vertical Excitation.** The $^1A'$ and $^3A'$ states of DMSO were found to correlate with the vertical $B_1$ states of the $C_{2v}$ geometry, as in $H_2SO$. In addition the $^1A''$ and $^3A''$ were found to correlate with the vertical $B_2$ states of $C_{2v}$ geometry. The $^1A''$ state was found to be 5 kcal/mol lower in energy than the $^1A'$ state. The first vertical triplet excited state ($^3A'$) lies at 109 kcal/mol (corresponding to a $\lambda_{max}$ of 261 nm) above the ground state at MCQDPT/6-311+G(3df)//CASSCF[14,10]/6-311+G(3df). The lowest lying singlet state ($^1A''$) is 132 kcal/mol above the $C_s$ equilibrium geometry ($\lambda_{max}$ = 217 nm). The $^1A'$ state was found lie 137 kcal/mol giving the absorption $\lambda_{max}$ = 209 nm. The values are in good agreement with the experimental absorption spectrum that has been deconvoluted producing two bands with $\lambda_{max}$ at 205 nm and 219 nm.[54]

**Relaxed Excited State Geometries of DMSO.** Applying what was learned from the excited states of $H_2SO$, DMSO was evaluated similarly. Based on ground state calculations, the neglect of p-polarization on hydrogen by use of 6-311+G(3df) should not have a pronounced affect on the energetics. The excited singlet stationary structures for DMSO are shown above in Figure 17.

Four excited singlet state optimized geometries were located for DMSO (Figure 17). Again, hessians were attempted without success to classify these structures as minima on the excited state potentials. Two excited state geometries were located with $C_s$ symmetry and two were located with $C_{2v}$ symmetry. Structures **20 $^1A'$** and **20 $^1A''$** are almost the same in geometric shape. All of the bond distances are within a hundredth of an Angstrom and bond angles are within one degree. The structures, compared to ground state **20**, have much longer S-O bond lengths. All other bond angles and lengths are unremarkable for **20 $^1A'$** and **20 $^1A''$** (Figure 17).

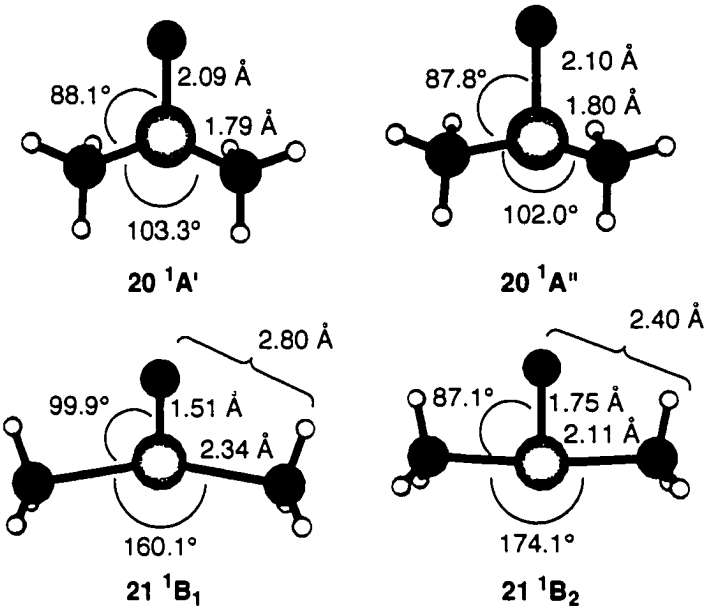



**Figure 17**. Singlet state relaxed geometries for DMSO calculated at CASSCF[14,10]/6-311+G(3df) Braces are showing H-O bond distances.

The structures located with $C_{2v}$ symmetry (Figure 17), **21** $^1$**B$_1$** and **21** $^1$**B$_2$**, are very comparable to **19** $^1$**B$_1$** and **19** $^1$**B$_2$** (Figure 6), respectively. With excited state **21** $^1$**B$_1$**, the S-O bond length is fairly normal, whereas the S-C bond is greatly lengthened and the HSH bond angle is deformed about 60° from the ground state molecular structure. With **21** $^1$**B$_2$** being T-shaped, the HSH bond angle is nearly linear (174°) and the S-O bond length is much longer than normal (0.23 Å longer than in ground state **21**). The major geometric differences between **21** $^1$**B$_1$** and **21** $^1$**B$_2$** are the much longer S-O bond and wider HSH bond angle in **21** $^1$**B$_2$**.

Two bound triplet structures were located and both had $C_{2v}$ symmetry. Figure 18 shows all four stationary excited structures, the two sulfoxides in $C_s$ symmetry are obviously unbound as the S-O bond lengths are about 4 Å. Again the bound $C_{2v}$ triplet structures, **21** $^3$**B$_1$** and **21** $^3$**B$_2$**, for DMSO are very similar to the bound triplet structures, **19** $^3$**B$_1$** and **19** $^3$**B$_2$**, for $H_2SO$, respectively. Structures **21** $^3$**B$_1$** and **21** $^3$**B$_2$** are also very comparable to the singlet excited geometries of **20** $^1$**A'** and **20** $^1$**A"**, respectively. Structure **21** $^3$**B$_2$** has the most linear CSC bond angle out of all of the structures located

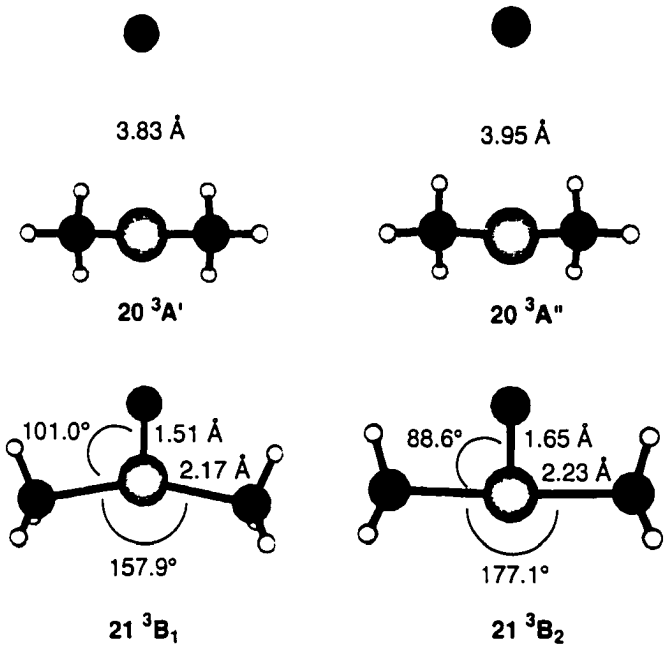



**Figure 18.** Triplet state relaxed geometries for DMSO calculated at CASSCF[14,10]/6-311+G(3df)

for either $H_2SO$ or DMSO. The CSC bond angle is 177°. As with the singlets, the S-O bond length is longer in **21** $^3\mathbf{B_2}$, but different than with singlets, in that **21** $^3\mathbf{B_2}$ has a longer C-S bond than **21** $^3\mathbf{B_1}$.

**Relaxed Geometry Energetics for DMSO**. The relaxed energetics for DMSO were calculated at the CASSCF[14,10]/6-311+G(3df) and MCQDPT/6-311+G(3df)//CASSCF[14,10]/6-311+G(3df) levels of theory. Figure 19 presents the results at the and MCQDPT/6-311+G(3df)//CASSCF[14,10]/6-311+G(3df) levels of theory and basis set. As with $H_2SO$, the CASSCF theory gave values some 20 kcal/mol higher for all of the states relative to the equilibrium ground state of DMSO than did the MCQDPT theory. As with $H_2SO$, the $C_s$ excited states were switched with **20** $^1$**A'** being higher in energy that with **20** $^1$**A"**, but at the MCQDPT level of theory **20** $^1$**A"** becomes lower in energy (5 kcal/mol) than **20** $^1$**A'**.

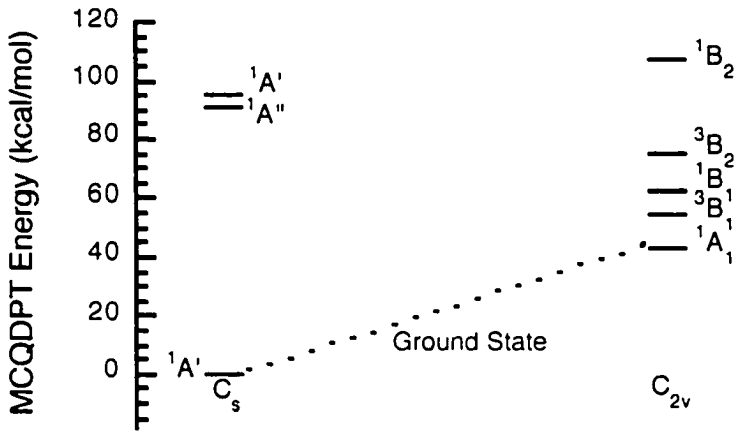



**Figure 19**. Energetics of relaxed geometries for DMSO at the MCQDPT/6-311+G(3df)//CASSCF[14,10]/6-311+G(3df) level of theory and basis set.

At the MCQDPT level of theory, structure **20** $^1$**A"** is 91 kcal/mol and structure **20** $^1$**A'** is 96 kcal/mol above the ground state **18**. These two relaxed geometries, **20** $^1$**A"** and **20** $^1$**A'**, correlate with relaxed geometries of **21** $^1\mathbf{B_2}$ and **21** $^1\mathbf{B_1}$, respectively. Structure **21** $^1\mathbf{B_2}$ is 16 kcal/mol higher in energy than **20** $^1$**A"**, where as **21** $^1\mathbf{B_1}$ is 35 kcal/mol lower in energy than **20** $^1$**A'**. These values are in qualitative agreement with the relaxed barriers observed with $H_2SO$ (Figure 10).

**Vertical geometry to relaxed geometry for DMSO**. A LLMP was constructed from **20** to each of the following geometries **21** $^1\mathbf{B_1}$, **21** $^1\mathbf{B_2}$, **21** $^3\mathbf{B_1}$, and **21** $^3\mathbf{B_2}$. Figures 20 and 21 show the energetics for the singlet and triplet pathways, respectively.

The LLMPs show that from the vertical excitation of **20** to both the singlet (Figure 20) and triplet (Figure 21) A' states a steady decline in energy to there respective relaxed structures, **21** $^1\mathbf{B_1}$ and **21** $^3\mathbf{B_1}$, on the $C_{2v}$ surface. The vertical excitation at the MCQDPT level of from **20** down to **21** $^1\mathbf{B_1}$ results in a 75 kcal/mol loss of energy. Convergence of the CASSCF wavefunction was again a problem the points closer to **21** $^1\mathbf{B_1}$ on the $^1$A' potential. The triplet surface shows a loss of energy (56 kcal/mol) from vertical excited **20** to relaxed **21** $^3\mathbf{B_1}$.

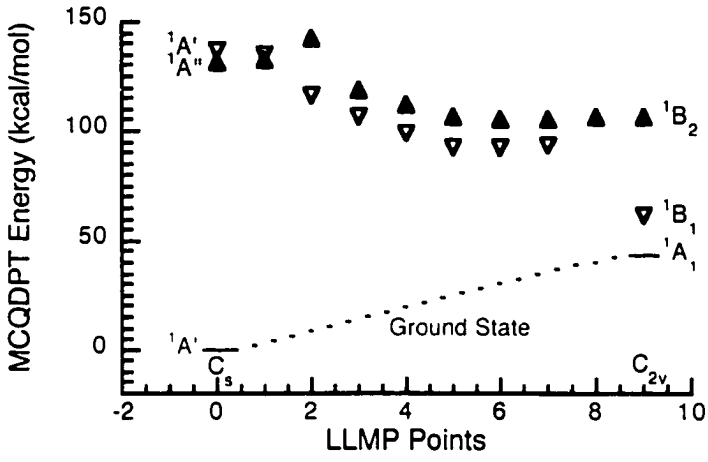



**Figure 20**. LLMP for DMSO singlet vertical to relaxed pathways.

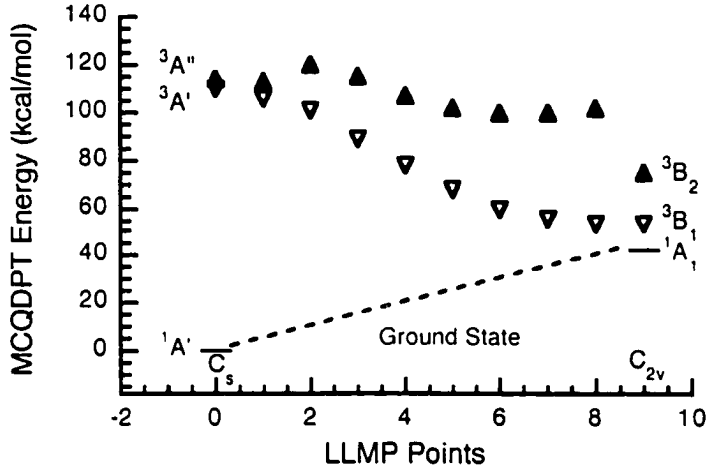



**Figure 21**. LLMP for DMSO triplet vertical to relaxed pathways.

Again as with $H_2SO$, both the singlet and triplet A" states are not well behaved. The vertically excited **20** does not proceed smoothly on the $^1$A" path down to relaxed **21** $^1\mathbf{B_2}$ (Figure 21). This also was the case for $H_2SO$, with a change in orbitals in going from points 2 – 4, indicated a forbidden crossing on the $^1$A" surface from another low lying $^1$A" state. A similar orbital change is observed

between points 2 – 4 on the triplet A" surface (Figure 21). The calculation of the states using state averaged orbitals for the two lowest lying A" states on the singlet surface led to a much smoother $^1$A" surface. The state averaged path was not calculated for the triplet pathway.

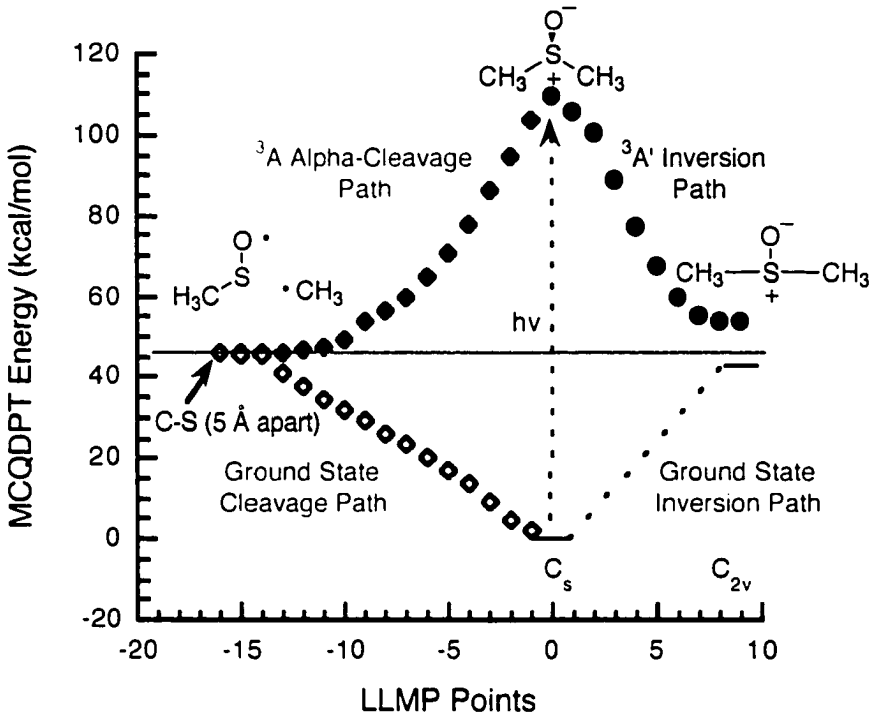



**Figure 22.** Triplet inversion and α-cleavage pathways for DMSO

**Inversion pathway versus α-cleavage pathway for DMSO**. The triplet inversion pathway is compared with the α-cleavage pathway above in Figure 22. The singlet α-cleavage pathway was attempted, but due to the loss of symmetry in going from $C_s$ to $C_1$ symmetry, convergence on the first $^1$A excited state was not possible. The α-cleavage LLMP was build after a C-S bond separation constrained optimization of ground state DMSO. The methyl radical and methane sulfinyl radical were separated by 0.05 Å for the first few tenths of angstroms. Then the C-S distance was gradually increased by larger increments until the radical pair was 5 Å apart to give the ground state cleavage path. After achieving the constrained optimized 5Å geometry, that geometry was connected with **21** and a LLMP was built to give the excited state path.

The triplet pathway of α-cleavage is shown to proceed smoothly from the vertical excited $^3A'$ **20** down the $C_1$ surface (red pathway in Figure 22). The energy loss in going from the triplet vertical state down to the radical pair at 5 Å apart is 64 kcal/mol, where as the 56 kcal/mol is lost during the inversion process (black pathway). From the C-S constrained optimization an estimate of the C-S bond strength can be made (green pathway). The value calculated at MCQDPT/6-311+G(3df)//CASSCF[14,10]/6-311+G(3df) levels of theory and basis set with the C-S bond at 5 Å is 46.0 kcal/mol. This value (46.2 kcal) essentially does not change even when the C-S bond is constrained at 20 Å. The C-S bond strength in DMSO has been calculated at the G2(MP2) level to be 53 kcal/mol and measured experimentally to be 53 kcal/mol[55], so the results from above are a few kcal/mol too low.

## Discussion

**Ground state inversion**. The inversion barriers and geometries at the MP2/6-311+G(3df,2p) level of theory and basis set for $H_2SO$ and DMSO compared well with those of Fueno et al.[13] The small differences in the inversion barrier as calculated by Fueno and co-workers lies in the smaller basis sets used for $H_2SO$ and DMSO (6-311+G(2d,p) and 6-31+G(2d), respectively). It was found that treatment of the inversion process with more sophisticated electron-correlation method produced better barrier energetics. For both $H_2SO$ and DMSO, after the MCQDPT correction was applied, the energies were greatly lowered (~10 kcal/mol) compared to the MP2 levels. For both of the different DMSO's geometries, i.e. MP2/6-311+G(3df) and CASSCF[14,10]/6-311+G(3df), used for the single point calculations at the MCQDPT level of theory produced inversion barriers in agreement with those determined experimentally for diaryl and alkyl aryl sulfoxides by Mislow and co-workers (41.5 and 43.6 (calculated this work) and 36-42 kcal/mol (experiment)).[6]

**Excited state inversion**. Both $H_2SO$ and DMSO produced similar excited state pictures. From the vertical excitation $H_2SO$ calculations, we gained the correlation of states that allowed hope for location of a stationary point on the excited state potential. After many trials and tribulations, the excited state optimizations proved fruitful. This allowed the construction of LLMPs that would not have been possible without locating stationary points on the excited state potentials. All attempts at

running intrinsic reaction coordinate (IRC) calculations on the excited state surface were failures. This can be attributed to the lack of the use symmetry that is necessary for the IRC steps.

The excited state relaxed geometry to relaxed geometry LLMP provided that small barriers may exist on the excited state potentials of simple sulfoxides. Even though these barriers are shown to exist, they more than likely do not play a role in the chemistry observed by photochemists.

One of the most intriguing results is the geometry of the excited state structures. The fact that the sulfoxides can undergo such geometry deformations is remarkable considering the weak C-S bond. This bond has been estimated by Benson and co-workers to be 55 kcal/mol[56] and determined from experiment to be 53 ± 2 kcal/mol by Zhao and co-workers.[55] These same workers also determined the C-S bond strength from a G2(MP2) calculation (52.6 kcal/mol).[55]

The vertical excitation of the $C_s$ ground state geometry was found to correlate to a $C_{2v}$ relaxed geometry (a T-shaped geometry) much lower in energy. It is interesting to postulate the edge inversion mechanism[57] instead of the normal pyramidal inversion mechanism in the excited state formation of the T-shape $C_{2v}$ geometries. These T-shaped structures have been observed previously with special sulfuranyl radicals.[53]

One of the fundamental questions that we asked when starting this computational study was, will a stationary point on the excited state potential be accessible from relaxation from the initial vertical excited state? Indeed, from the vertical excitation for both $H_2SO$ and DMSO, relaxation can occur with littler or no barrier to an almost T-shape geometry state for both the singlet and triplet surfaces (Figures 14, 15, 20, and 21). From the T-shape stationary point the sulfoxide can partition to the left or right side of the thermal transition state to form a racemic mixture (i.e. if the sulfoxide is chiral).

Lee and Jenks have proposed a mechanism for photoracemization of aromatic sulfoxides consistent with inversion occurring out of the singlet manifold.[26] Our group also has proposed that majority of inversion proceeds without bond scission unless the C-S bond weakened by substituents that form stable radicals.[36] The fact that our calculations suggest this T-shaped stationary point on the excited state potential. It cannot be shown directly if the photoracemization is occurring first through pyramidal inversion then to the T-shape molecule or from edge inversion directly since the

IRC would not run. Regardless of the mechanism in forming the relaxed T-shape geometry, the fact the computations predict such a state is consistent with the suggestion of Schlessinger and Schultz[34,58] and Kropp and co-workers.[35] This study motivates one to examine a prototypical aromatic sulfoxide structure (e.g. PhS(O)Me) for which experiments have been completed.

Lastly, does the α-cleavage mechanism compete with the inversion mechanism? Figure 22 does not provide a definitive answer, at least on the triplet surface. Even though the recent evidence is against photoinversion out of the triplet manifold in aromatic sulfoxides,[26] if the triplet vertical state could be accessed, then DMSO complete between the α-cleavage or the inversion pathways. Our calculations probably biased this result since it was required that the LLMP was constructed using the vertical state as the starting structure. However, nothing required the first α-cleavage point to smoothly proceed down from the vertical $C_s$ point. As a matter of final note, the energy of C-S bond in DMSO was predicted to be only worth 46.2 kcal/mol that is quite different from the one determined experimentally or by G2(MP2) (53 kcal/mol).[55] This value can be improved to 48.4 kcal/mol if the MCQDPT/6-311+G(3df,2p)//MP2/6-311+G(3df,2p) energy is used. At this time there is no other explanation to be offered for this discrepancy.

## Conclusions

From this excited state study, the first computational prediction of excited state geometries of sulfoxides was shown. A T-shaped stationary point on the excited state potential from vertical relaxation without barrier is proposed for photoinversion without C-S bond scission being necessary. The structure of this state could have possibly come from either pyramidal or edge photoinversion. Inversion was calculated out of the triplet state to be able to compete equally between α-cleavage or photoinversion.

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# CHAPTER 4

# BIMOLECULAR PHOTOREDUCTION OF AROMATIC SULFOXIDES

A paper to be submitted to the *Journal of Organic Chemistry*[1]

Jerry W. Cubbage, Troy A. Tetzlaff, Heather Groundwater, and William S. Jenks

## Introduction

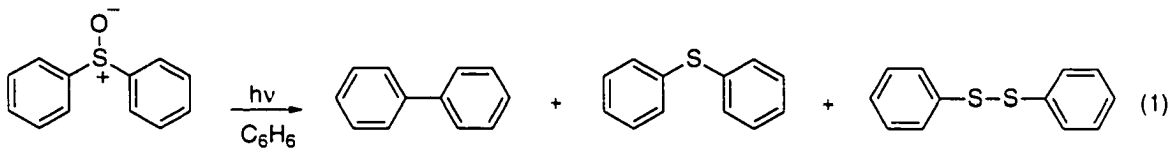
The reduction of the sulfoxide functional group has received a great deal of attention in the past thirty years. There have been many exhaustive reviews of various reagents to achieve this reduction.[2-7] Inevitably, some reagents are more gentle or well suited to certain functionalities than others. The photochemical reduction of sulfoxides, however, has not received a great deal of attention.

Most references to unassisted (unimolecular) photochemical sulfoxide reduction show the reaction producing several different products. The appearance of reduction product sulfide varies in concentration from major to minor, contingent upon starting material and reaction conditions. In addition, the products of photolysis are unpredictable. In general, it is not a synthetically useful reaction. This chapter will show that reduction can be made predictable. For the purposes of this review, only a selected sampling of these direct and sensitized photochemical reactions will be examined. For a more detailed review of the literature refer to Jenks et al.[8]

Unlike the unassisted photochemical reaction, the photoassisted reaction produces sulfide as the major and often sole product. This reaction is unusual for sulfoxide photochemistry in that it appears to be a bimolecular reaction. A key step of the reaction appears to be the transfer of an electron to the sulfoxide functional group. Subsequent steps lead to the formation of sulfide. A large increase in the yield and efficiency of sulfide production compared to the unassisted reaction, as well

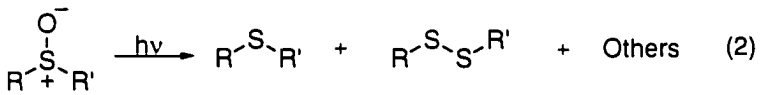
as an increase in product selectivity, makes the photoassisted process more appealing for synthetic purposes than the unimolecular reaction.

An early example of an unassisted reduction of a sulfoxide to sulfide is by Kharasch and Khodair.[9] They examined the direct photolysis of diphenyl sulfoxide **1** in benzene (equation 1). It was observed that photolysis produced 53% biphenyl **2**, 7% diphenyl sulfide **3** and a small amount of diphenyl disulfide **4** as products. This is a good example of a reaction that produces multiple products with sulfide only as a minor photolysis product.



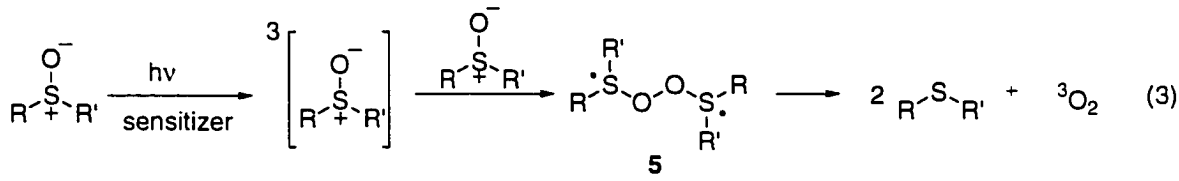

**1** **2** **3** **4** (1)

Shelton investigated the photolysis of several dialkyl and alkyl aryl sulfoxides under direct and sensitized photolysis in benzene.[10] The general reaction is illustrated in equation 2. The photolysis of these sulfoxides generally results in the formation of sulfide as well as other products. The sulfide production ranges from major to minor depending on the structure of sulfoxide and photolysis conditions.

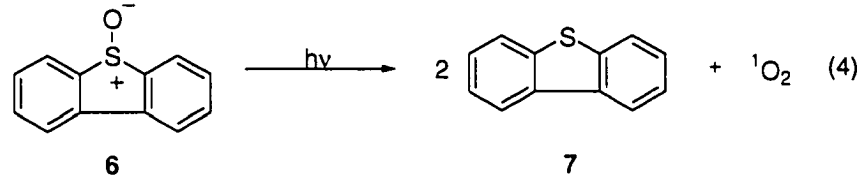



(2)

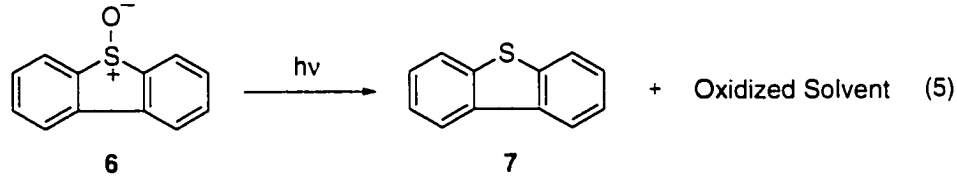
Shelton proposed a mechanism that explained the production of sulfide in cases when a sulfoxide disproportionation process (*i.e.* co-production of sulfone) was not observed. Shelton proposed a dimer type mechanism to explain this phenomenon, which the "dimer mechanism" is outlined in equation 3. This mechanism relies on the formation of the peroxy-type intermediate **5** from the coupling of a triplet excited and a ground state sulfoxide. This peroxy intermediate is then proposed to fragment into ground state sulfide and ground state molecular oxygen.[10]



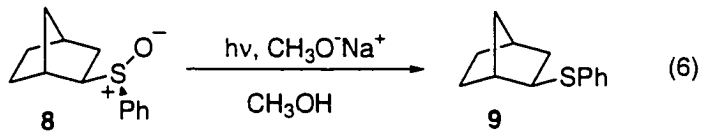

The work of Posner also implied an equivalent dimer mechanism.[11] Upon photolysis of dibenzothiophene oxide (DBTO) **6**, the deoxygenation product dibenzothiophene (DBT) **7** is produced (equation 4). In this case **7** is the primary photolysis product. Although the formation of a peroxy-type intermediate **5** is not explicitly stated, it is proposed that singlet molecular oxygen is produced.



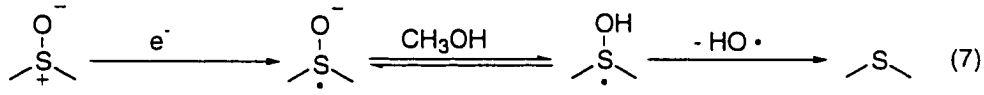

Recently, Jenks[12,13] proposed an alternative to the "dimer mechanism;" this work is shown in equation 5. These experiments resulted in the observation of **7** and oxidized solvent. The nature of the oxidizing agent is best described as an O atom, namely the ground state of molecular oxygen, O($^3$P). This oxidizing agent is proposed to originate by direct cleavage of the sulfur oxygen bond.




A photoassisted (bimolecular) mechanism to explain the results of a photochemical reduction reaction was proposed by Kropp.[14] The investigated photoreaction is viewed in equation 6. The photolysis of 2-norbornyl sulfoxide **8** in methanol produced only a trace amount of 2-norbornyl sulfide **9**. The yield of **9** increased to 64% upon the addition of 0.2 M sodium methoxide. The proposed mechanism involves the donation of an electron from sodium methoxide to the photo-excited state of




(6)




(7)

**8** (equation 7). Proton transfer from the solvent results in the intermediate hydroxy-sulfuranyl radical **10**. Subsequent loss of the hydroxyl radical produces the observed sulfide product.

Although other studies have suggested a single electron transfer mechanism to obtain sulfide,[2] no photochemical studies have approached the selectivity for sulfide production as reported by Kropp.[14] The bulk of the work in this chapter will concentrate on the investigation of Kropp's results, the exploration of his proposed bimolecular mechanism, and extension of this idea.

# Results

### Sodium methoxide/methanol solvent system

In order to replicate the results of Kropp,[14] where an alkyl phenyl sulfoxide (see equation 6) was studied, methyl phenyl sulfoxide **11** was chosen as starting material. Solutions of 10 mM **11** along with 1 mM p-xylene **12** (as an internal standard), and the desired concentration of sodium methoxide were prepared in HPLC grade methanol. Argon degassed samples of the solution were photolyzed in quartz test tubes. A Rayonet mini-reactor using broad band UV bulbs whose emission is centered at 300 nm was used for photolysis. Analysis was performed by HPLC.

A series of experiments in which the concentration of sodium methoxide was varied from 1 to 200 mM were undertaken. The results can be seen in Table 1. The general reaction can be observed in equation 8. It should be noted that at all times the control experiment (without sodium methoxide) produced only trace amounts of sulfide during photolysis. These data show that the yield of sulfide is enhanced with an increase in the concentration of sodium methoxide. The data also show that the production of sulfide appears not to be stoichiometric with respect to sodium

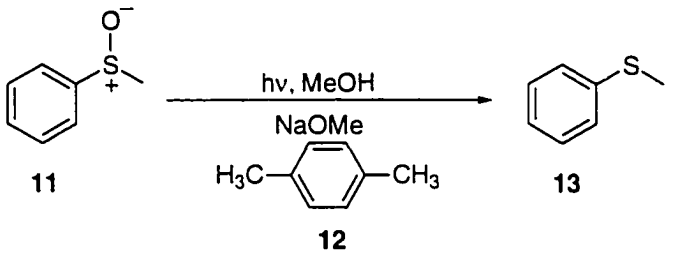



**Table 1.** Percent yield of methyl phenyl sulfide **13** as a function of sodium methoxide concentration in methanol at 300 nm.[a] The starting concentration of methyl phenyl sulfoxide was roughly 10 mM.

| | Sodium methoxide (mM) | | |
|---|---|---|---|
| Photolysis time (min) | 1 | 104 | 200 |
| 30 | 16 | 18 | 30 |
| 45 | 28 | | |
| 60 | 26 | 41 | 55 |
| 90 | 33 | 54 | 66 |
| 120 | 37 | 60 | 63 |
| 150 | 40 | 56 | |
| 170 | 42 | | |
| 200 | 43 | | |

[a]It is of note that an experiment run with 6 mM sodium methoxide present resulted in sulfide yields comparable to the 1 mM sodium methoxide experiment.

methoxide, in that only a 10% yield of sulfide could have been achieved with 1 mM sodium methoxide were that the case.

It was next determined if there was a requirement for an alpha hydrogen to the sulfoxide functional group. Diphenyl sulfoxide **1** was chosen as a prototypical example. Photolysis conditions and other experimental factors were identical to the methyl phenyl experiment. The production of **3** was again monitored by HPLC. The results for this set of experiments are listed in Table 2. A control experiment without base again indicated only a trace yield of sulfide. In this case, the percentage of converted starting material gives an indication of when the experiment is nearing completion and whether secondary photolysis is taking place. These data also show that there is no requirement for an alpha hydrogen to the sulfoxide in this reaction.

**Table 2.** Percent yield of diphenyl sulfide **3** and percent conversion of starting material as a function of sodium methoxide concentration in methanol at 300 nm. The starting concentration of sulfoxide was roughly 10 mM.

| Photolysis time | 1 mM NaOMe | | 200 mM NaOMe | |
|---|---|---|---|---|
| (min) | % yield | % conversion | % yield | % conversion |
| 30 | 25 | 43 | 78 | 93 |
| 60 | 41 | 58 | 58 | 97 |
| 90 | 43 | 72 | | |

Much like the photolysis for **11**, the experiments indicated an increase in the production of sulfide with an increase in base concentration. These data also showed that the production of sulfide is not stoichiometric with respect to sodium methoxide concentration.

In an effort to confirm the stoichiometry of the reaction, a large scale photolysis was undertaken. In this experiment, a solution of 82 mM **1**, 6 mM sodium methoxide, and 10 mM **12** (internal standard) was prepared. The solution was photolyzed for 18.5 hours and analyzed by HPLC chromatography. The experiment yielded 25% (20.5 mM) of compound **3**. If the reaction was entirely 1:1 in stoichiometry with regard to the concentration of sodium methoxide, only a 7% yield (6 mM) of **3** would have been expected.

**Sodium *tert*-butoxide/*tert*-butyl alcohol solvent system**

Up to this point in the investigation it is clear that sulfoxide is being reduced to the corresponding sulfide. It is postulated that since there are no other sulfur oxidation products, the solvent is being oxidized. This would most likely result in methanol being oxidized to formaldehyde.

To test this hypothesis, a photolysis system of *tert*-butyl alcohol and sodium *tert*-butoxide was used. The hypothesis is that since there is not an available alpha hydrogen next to the oxygen, *tert*-butyl alcohol would be more difficult to oxidize that methanol. This would then result in a decrease or stoppage of sulfide production. Reaction conditions were similar to the previous study except *tert*-butyl alcohol with 1% $H_2O$ (approximately 0.5 M) was used as solvent and sodium *tert*-butoxide was used as anion, meaning a mixture of hydroxide and *t*-butoxide was present. The results for this set of experiments are reported in Table 3. These experiments showed that the production of sulfide was

**Table 3.** Percent yield of diphenyl sulfide **3** and percent conversion of starting material as a function of sodium *tert*-butoxide concentration in *tert*-butyl alcohol at 300 nm. The starting concentration of sulfoxide was roughly 10 mM.

| Photolysis time | 83 mM *t*-BuONa | 160 mM *t*-BuONa |
|---|---|---|
| (min) | % yield of sulfide | % yield of sulfide |
| 0 | 0 | 0 |
| 30 | 9 | 8 |
| 60 | 15 | 13 |
| 90 | | 16 |
| 120 | | 14 |
| 150 | 20 | |

much lower compared to the system of sodium methoxide and methanol (Table 2). In addition, it was evident that the further addition of sodium *tert*-butoxide did not appear to increase the yield of sulfide.

In order to further investigate what was being oxidized, methanol was added to the *tert*-butyl alcohol system. This was done in anticipation of observing an increase in the yield of sulfide. The reaction conditions are similar to previous experiments except that the concentration of sodium *tert*-butoxide and methanol were varied while being dissolved in *tert*-butyl alcohol. The reaction conditions and percent conversions of the four sets of experiments are shown in Table 4. The data from the reactions can be observed in Figure 1. In general, these experiments showed that using methanol as an additive to the *tert*-butyl alcohol system greatly increased the yield of sulfide compared to when methanol was not present.

**Table 4.** Percent conversion of diphenyl sulfoxide **1** as a function of photolysis time for Systems I-IV. The starting concentration of sulfoxide was 10 mM.

| System | I | II | III | IV |
|---|---|---|---|---|
| [Methanol] , mM | 0 | 81 | 41 | 164 |
| [Sodium *tert*-butoxide], mM | 162 | 80 | 160 | 67 |
| Photolysis time (min) | Percent conversion of sulfoxide | | | |
| 30 | | 44 | 51 | 79 |
| 60 | 51 | 62 | 70 | 97 |
| 90 | 60 | 74 | 78 | |
| 120 | 59 | | | |

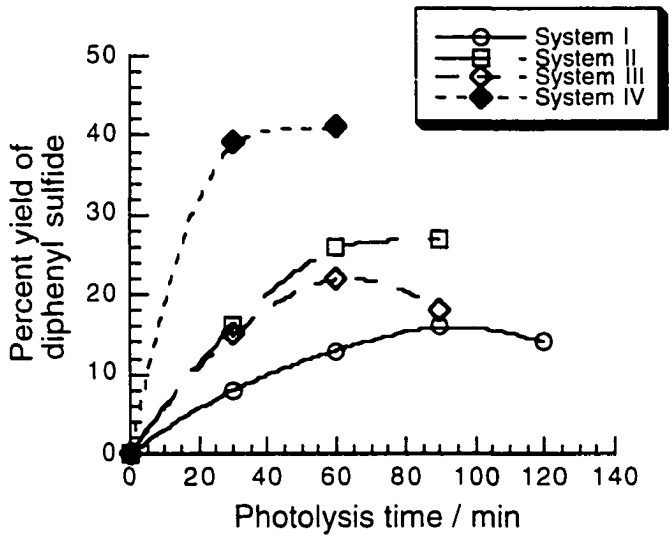



**Figure 1.** Yield of diphenyl sulfide **3** as a function of photolysis time for systems stated in Table 4.

The next series of experiments were similar to the previous study. In this case, *tert*-butyl alcohol contained 1% ethyl ether, and not 1% water as an additive as had been used in the previous experiments. The results of these experiments can be seen in Table 5 and Figure 2. The results showed that the addition of methanol to this system had no effect on the production of sulfide.

**Table 5.** Percent conversion of diphenyl sulfoxide **1** as a function of photolysis time for Systems V-VIII. The starting concentration of sulfoxide was 10 mM.

| System | V | VI | VII | VIII |
|---|---|---|---|---|
| [Methanol] , mM | 0 | 80 | 160 | 320 |
| [Sodium *tert*-butoxide], mM | 180 | 180 | 180 | 180 |
| Photolysis time (min) | Percent conversion of sulfoxide | | | |
| 30 | 34 | 42 | 45 | 51 |
| 60 | 60 | 66 | 74 | 80 |
| 90 | 86 | 83 | 86 | 95 |
| 120 | 94 | | | |

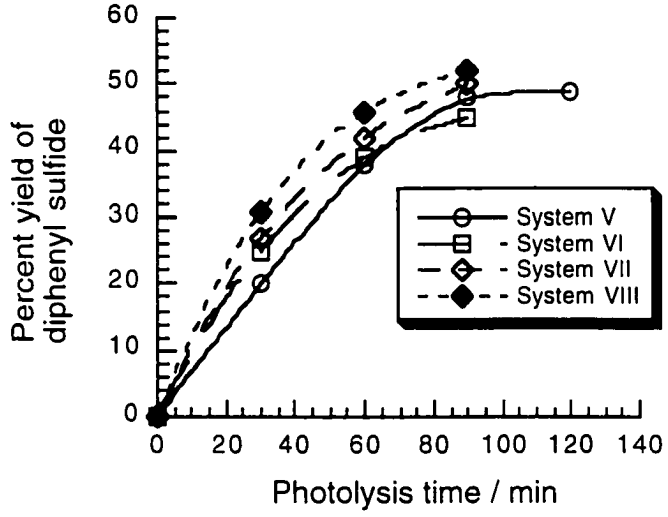



**Figure 2.** The effect of adding methanol to the sodium *tert*-butoxy and *tert*-butyl alcohol (1% ether) systems is shown in Table 5.

Furthermore, it was observed that the production of sulfide when methanol was not present within this system was much higher when compared to the sodium *tert*-butoxide system using *tert*-butyl alcohol with 1% water spike.

To determine if the addition of water to the system had an effect on the production of sulfide, a series of experiments were undertaken. In this example, both the sodium methoxide/methanol and sodium *tert*-butoxide/*tert*-butyl alcohol systems were compared. The experiments were performed by constructing solutions of 10 mM **1**, 150 mM sodium methoxide or sodium *tert*-butoxide, and 1 mM **12** (as an internal standard). To these stock solutions was added 360 mM water. The samples were then prepared, photolyzed, and analyzed as previously. The results of these experiments are listed in Tables 6 and 7. These data show that the addition of water has no observed effect on the sulfide production for both systems.

**Table 6.** The yield of diphenyl sulfide **3** as a function of added water to the methanol / sodium methoxide system.

| Photolysis time (min) | 150 mM NaOMe, 0 mM water<br>150 mM base : 360 mM water | | 150 mm NaOMe, 360 mM water | |
|---|---|---|---|---|
| | % yield | % conversion | % yield | % conversion |
| 30 | 61 | 85 | 45 | 92 |
| 60 | 69 | 98 | 69 | 98 |

**Table 7.** The yield of diphenyl sulfide **3** as a function of added water to the *tert*-butyl alcohol / sodium *tert*-butoxide system.

| Photolysis time (min) | 180 mM t-BuONa, 0 mM water<br>150 mM base : 360 mM water | | 180 mm t-BuONa, 360 mM water | |
|---|---|---|---|---|
| | % yield | % conversion | % yield | % conversion |
| 30 | 20 | 33 | 18 | 26 |
| 60 | 33 | 65 | 29 | 33 |

The final investigations at 300 nm involved the examination of other common anions to ascertain if they could be applied to this reaction. The anions that were studied were sodium methoxide (control), potassium chloride, potassium bromide, and potassium iodide. Samples were prepared and analyzed by the conditions explained previously. It was observed that the only anion other than methoxide to show any measurable yield of **3** was iodide. Even in this case the formation of sulfide was only in trace amounts after 90 minutes of photolysis.

**Experiments at 254 nm**

In order to measure the quantum yield of the photoreduction of a sulfoxide to sulfide, photolyses were undertaken at 254 nm. This wavelength was chosen over 300 nm because the low pressure mercury lamp used in these experiments has a well defined Hg emission line at 253.7 nm. The 300 nm bulbs have a broad band emission centered at 300 nm and therefore do not apply well to quantum yield measurements.

It was also necessary to run the quantum yield experiments to low conversion of starting material to reduce the likelihood of secondary photolysis. The threat of secondary photolysis can be seen by examining the extinction coefficients of starting material and some potential products listed in Table 8. Sulfoxide **1** absorbs light out to 310 nm and at 300 nm has an extinction coefiecient on the

order of 200.[8] Since compound **3** has a larger extinction coefficient than the sulfoxide **1** at 254 nm the reaction must be run to low conversion of starting material to avoid secondary photolysis of sulfide **3**. Secondary photolysis would occur when the concentration of **3** became large enough that it would absorb light.

**Table 8.** Extinction coefficients of relevant compounds.

| Compound | Extinction coefficient at 254 nm ($L\ mol^{-1}\ cm^{-1}$) |
|---|---|
| $Ph_2SO$ (**1**) | 2940 |
| $Ph_2S$ (**3**) | 11400 |
| $Ph_2$ | 19200 |
| PhSH | 2630 |

Due to the requirement for the experiment to be run to low conversion of starting material, only one or two 4 watt 254 nm bulbs were used for the photolyses; other bulbs were removed from the photoreactor or covered with aluminum foil. Samples, prepared as before, contained compound **1**, internal standard **12**, sodium methoxide and methanol. The results of the photolyses at 254 nm are shown in Figure 3. This experiment shows an induction period at low conversion, followed by a linear growth of sulfide concentration. This induction period will be discussed later.

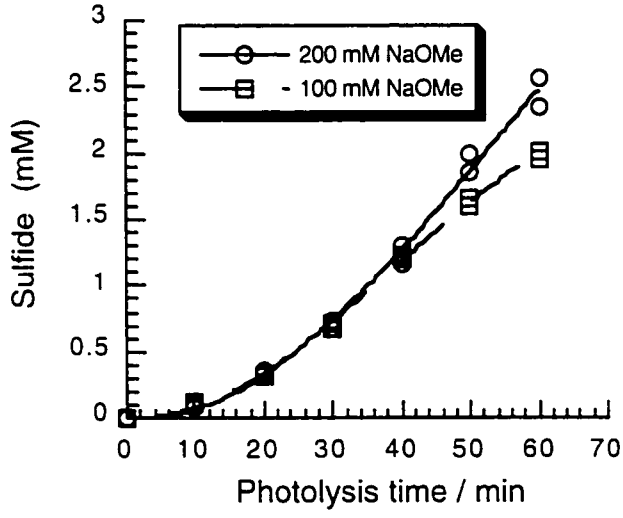



**Figure 3.** Yield of diphenyl sulfide **3** at 254 nm with low conversion of starting material.

**Effect of oxygen**

Experiments were undertaken to determine the effect of oxygen of **1**. In a pair of control experiments, a sample was deoxygenated by argon degassing; in the other experiment the sample was saturated with oxygen by bubbling with oxygen gas. Both were photolyzed at 254 nm with either two and four bulbs to vary the conversion of starting material. Although the concentration of major products, such as diphenyl sulfone and phenol varied, the formation of diphenyl sulfide was observed only in trace amounts.

The next experiment examined the effect of oxygen on the production of sulfide when sodium methoxide was present. This experiment involved the coincident photolyses of two identically constructed solutions of 10 mM **1**, 2 mM **12**, and 200 mM sodium methoxide. The difference in the two samples was that one was argon degassed, while the other was oxygen saturated. These samples were then photolyzed at 254 nm and monitored by HPLC. The results of this experiment can be seen in Figure 4. The data showed that the presence of a large amount of oxygen within the sample quenches the reaction or severely retards the formation of sulfide. It should also be noted that in the presence of oxygen the consumption of sulfoxide is also severely slowed down, and there was not a noticeable formation of any other major photolysis products.

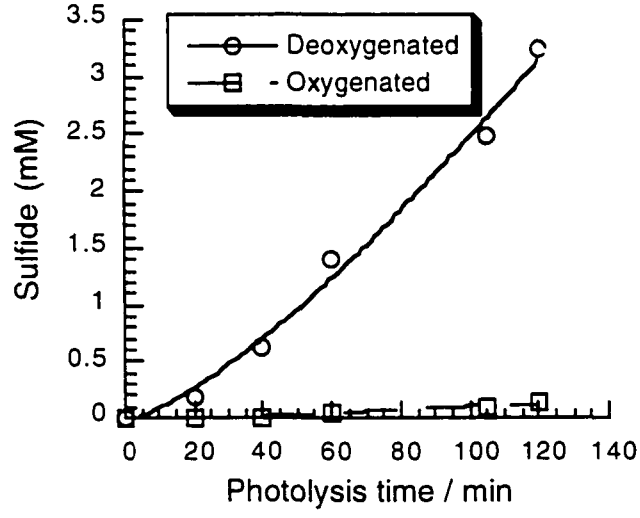



**Figure 4.** Effect of oxygen on the production of diphenyl sulfide **3** at 254 nm.

For proper quantum yield measurements, zero order kinetics without an induction period are required. Freeze-pump-thaw (FPT) experiments were performed to investigate the induction period at low conversion, as seen in Figure 3. It was initially thought that the induction period was caused by residual oxygen in the sample, therefore the FPT method was employed to remove the oxygen. The FPT method of deoxygenation involves freezing the sample with liquid nitrogen and evacuating. Subsequent cycles of thawing the liquid, refreezing and evacuating is an efficient method for removing oxygen and other gases from a sample. The experimental sample was prepared as before, except that the sample was placed in a quartz tube with a specially outfitted side arm for vacuum degassing. After the sample had been through sufficient FPT cycles to show no change in pressure, it was photolyzed at 254 nm. Results for this experiment are shown in conjunction with an argon degassed sample with the same concentration of sodium methoxide. These results are presented in Figure 5. These data showed that the induction period is not reduced upon FPT photolysis.

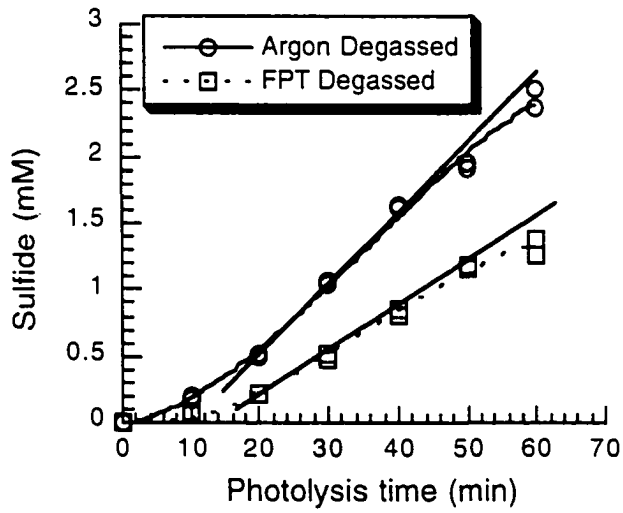



**Figure 5.** The effect of a FPT experiment on the observed induction period at low conversion of diphenyl sulfoxide **1** at 254 nm. An example of the line used to calculate approximate quantum yields is also shown for these experiments.

It was suspected that the induction period might come from impurities. To try to eliminate that, freshly prepared sodium methoxide and diphenyl sulfoxide **1** (multiply recrystallized four times from hexanes) was used. The preparation of the sodium methoxide solution consisted of dropping clean pieces of sodium in methanol. Sodium was cleaned by three consecutive washings in methanol, drying, and quickly weighing. This solution was allowed to cool to room temperature before the addition of other reagents. The UV spectra were taken for both commercial and freshly prepared sodium methoxide. It was found that the freshly prepared sodium methoxide solution contained no significant absorbance down to below 240 nm, whereas sodium methoxide purchased from Mallinckrodt contained an absorbance from an impurity (Figure 6).

Using the freshly prepared sodium methoxide (200 mM), recrystallized diphenyl sulfoxide **1** (10 mM), and dodecane (6.18 mM) as an internal standard, a solution in methanol was constructed. This solution (100 mL) was put into a quartz reactor, equipped with a septum, and flushed with argon for 20 minutes. This solution was then photolyzed for 180 minutes at 254 nm (2 bulbs in mini-reactor). Samples of 0.5 mL were collected every ten minutes,

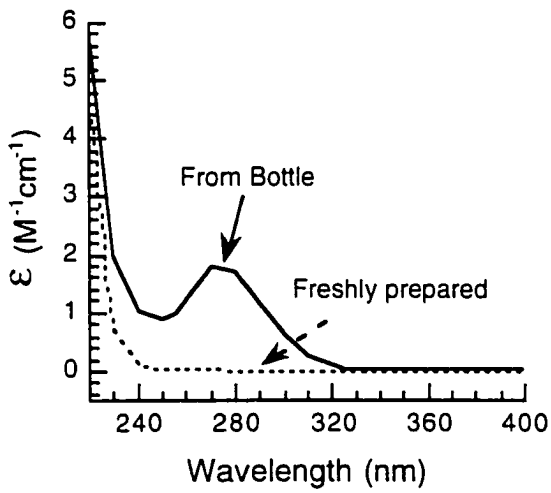



**Figure 6.** Absorption spectra of sodium methoxide in methanol from bottle (solid line) and freshly prepared (dotted line).

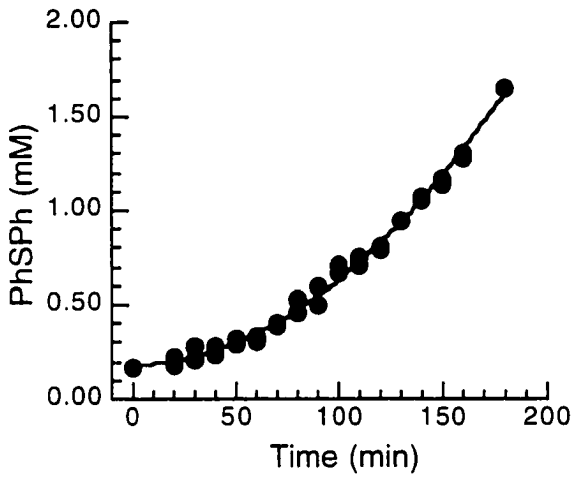



**Figure 7.** The effect of using freshly prepared sodium methoxide on the observed induction period at low conversion of diphenyl sulfoxide **1** at 254 nm.

diluted with water (0.5 mL) and exctracted with ether (1.0 mL). The ether extract was then analyzed by GC. The results and the ever so present induction period are shown in Figure 7.

**Quantum yield experiments**

In order to achieve an understanding of how much the efficiency of the photoassisted reaction has increased relative to the unassisted reaction, quantum yields must be obtained. By definition, quantum yields represent how many events occur from the absorbance of a photon. In other words, a quantum yield represents an efficiency of a reaction related to the number of photons absorbed. The equation to calculate quantum yield in which all light is absorbed is shown in equation 9

$$\Phi \equiv \frac{C}{T} \bullet \frac{V}{I_0} \qquad (9)$$

where, $\Phi$ represents the quantum yield of the reaction, $I_o$ represents the photon flux of the light source (how many photons are emitted per minute), C is the molar concentration of starting material, V is the sample volume in liters, and T is the photolysis time in minutes. In order to obtain a quantum yield value, the linear slope of a concentration versus time plot at low conversion (e.g. Figure 5) is

corrected for sample volume and $I_o$. To obtain a value for $I_o$, azoxybenzene was used as an actinometer.[15] To obtain the linear slope of sulfide formation, the induction period was ignored. The resulting data was used to approximate a linear slope as shown in Figure 5.

*Samples of 10 mM compound* **1**, *3 mM compound* **12**, *and varying amounts of sodium* methoxide were photolyzed at 254 nm. The quantum yield for the disappearance of **1** and the appearance of **3** are shown in Table 9. The data listed within Table 9 are averages of at least two separate quantum yield experiments. These data show that the addition of a large excess of sodium methoxide increases the quantum yield of sulfide production. At 200 mM sodium methoxide, the yield of appearance of 0.045 indicates a maximum yield of 50% sulfide.

**Table 9.** Quantum yields examining diphenyl sulfoxide at 254 nm.

| Sodium methoxide (mM) | Quantum yield of disappearance of sulfoxide | Quantum yield of appearance of sulfide |
|---|---|---|
| 200 | 0.103 | 0.045 |
| 100 | 0.079 | 0.035 |
| 50 | 0.047 | 0.037 |

**Table 10.** Quantum yields examining DBTO at 254 nm.

| Sodium methoxide (mM) | Quantum yield of disappearance of sulfoxide **6** | Quantum yield of appearance of sulfide **7** |
|---|---|---|
| 200 | 0.110 | 0.062[a] |
| 100 | 0.169 | 0.079[a] |
| 50 | 0.081 | 0.047 |
| 25 | 0.123 | 0.049 |
| 6 | 0.140 | 0.029 |
| 0 | | 0.013 |

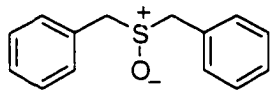
[a] Significant run to run data scatter was observed for these concentrations.

**Other sulfoxides studied**

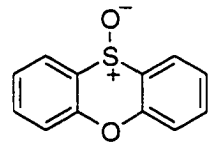
The quantum yields of dibenzothiophene oxide **6** (DBTO) were then investigated to examine if the quantum yield for deoxygenation of sulfoxide would be increased from the unassisted value of 0.013. Samples were prepared identically to the previous experiment and photolyzed at 254 nm. The quantum yields for the disappearance of DBTO and the appearance of **7** (DBT) are shown in

Table 10. The data listed within Table 10 are averages of at least two separate quantum yield experiments. These data show that there is a large increase in the quantum yield of sulfide using the photoassisted reaction compared to the unassisted (0 mM sodium methoxide) experiment.

Other sulfoxides were also qualitatively investigated to discover if the addition of sodium methoxide would increase the production of sulfide. The sulfoxides studied were dibenzyl sulfoxide **14**, and phenoxathiin oxide **15**. Solutions of 10 mM compound **14** or **15**, and approximately 200 mM sodium methoxide were prepared as before and photolyzed at 254 nm. The results of these experiments showed that **14** did not have a noticeable increase in the production of sulfide. However, compound **15** did show an enhancement of the sulfide yield over the control experiment i.e., the experiment without sodium methoxide.



**14**

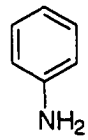


**15**

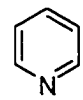
**Other electron donors and sensitized photolysis conditions**

**Pyridine versus aniline**

A set of experiments that utilized aniline **16**, and pyridine **17** was undertaken to try to distinguish basicity from electron donation as a key factor. Since the $pK_B$ values of the two bases are similar, 9.4 for the former and 8.8 for the latter,[16] both compounds would be expected to deprotonate methanol in similar, but small, amounts compared to directly using sodium methoxide.



**16**



**17**

Samples were prepared with 10 mM **1**, 3 mM xylenes as internal standard and 100 mM of the amine in methanol. The argon degassed samples were photolyzed as before in quartz test tubes at 254 nm. The addition of **16** to the photolysis system provided sulfide. On the other hand, the addition of pyridine showed no observable increase in production of **3** above the control values.

In light of the aniline result, other amines studied include the following: aniline **16**, N-methyl aniline **20**, N,N-dimethyl aniline **21**. It was hypothesized that oxidation of the methylated anilines to anilinium salts might occur. It was found that irradiation could be concentrated on the aniline, rather than the sulfoxide. This turns the reaction into a sensitized one from the perspective of the sulfoxide. Photolyses were carried out at 300 nm for anilines, to ensure that the majority of light is being absorbed by the aromatic amine. All photolyses were analyzed by GC with dodecane as an internal standard.

One experiment with methyl phenyl sulfoxide **11** (10 mM), with aniline **16** (0.5 mM), and dodecane (5.0 mM) in methanol was carried out. Three solutions were constructed to investigate the effect of oxygen saturation, air saturation, and argon saturation on the reduction process. The argon flushed sample produce the highest yield of sulfide (70% yield at 70% conversion of sulfoxide) at 120 minutes. Both the air and oxygen saturated samples had much lower yields of sulfide, in agreement with previous experiments in which the sulfoxide had absorbed the light.

The rest of the reductions in this section were run with diphenyl sulfoxide **1**. Two samples were prepared containing **1** (10 mM), dodecane (5.0 mM) and one with N-methyl aniline **20** (10 mM) and the other with N,N-dimethyl aniline **21** (10 mM). Each sample was photolyzed at 300 nm and analyzed via GC at 60 and/or 120 minutes. The results from these experiments are shown in Table 12. No aniline demethylation products (e.g. aniline from N-methylaniline) were observed.

**Table 12.** The yield of diphenyl sulfide **3** with N-methyl aniline **20** and N,N-dimethyl aniline **21** electron donors.

| Photolysis time | 10 mM **20** | | 10 mM **21** | |
|---|---|---|---|---|
| (min) | % yield | % conversion | % yield | % conversion |
| 60 | 68 | 78 | | |
| 120 | 85 | 85 | 65 | 65 |

**Solvent effect with N-methyl aniline**

The effects of solvent on the reduction process with the aniline systems were evaluated. The reduction of diphenyl sulfoxide **1** with N-methyl aniline **20** in methanol spiked with 1% water, in dry THF, and in THF spiked with 1% water. The samples contained **1** (10 mM), **20** (10 mM), and dodecane (5.0 mM) in the respective solvent. Each sample was photolyzed (@ 300 nm) for 120 minutes and all produced sulfide. The sample with methanol spiked with water produced sulfide in 90% yield at 90% conversion, whereas the dry THF solution only produced 58% sulfide at 90% conversion. The wet THF sample was only marginally better than the dry THF sample (66% yield of sulfide at 90% conversion). The wet methanol solution was the best solvent system for producing sulfide. However, comparative yields were observed with the methanol without water system in Table 12.

Quantum yields for diphenyl sulfide apperance with N-methyl aniline **20** as an electron donor as a function of solvent were determined. No induction period was observed. Samples containing **1** (10 mM), **20** (10 mM), and dodecane (5.0 mM) in of the following solvents methanol, acetonitrile, or THF were prepared. The quantum yields for appearance of sulfide are shown in Table 13. All quantum yields were determined at less than 10% conversion of sulfoxide and from duplicate runs. Azoxybenzene was used as an actinometer and photolysis was carried out at 313 nm to insure anilines absorbed the light. The use of methanol as solvent produced the highest quantum yield of sulfide **3**.

**Table 13.** Quantum yield of the appearance of diphenyl sulfide **3** with N-methyl aniline **20** as electron donor

| Solvent | Quantum yield of appearance of sulfide[a] |
|---|---|
| MeOH | 0.48 |
| MeCN | 0.34 |
| THF | 0.41 |

[a]Estimated error limits of quantum yields are 20% and values are from the average of two duplicate runs.

**Carbazoles as reducing agents**

Carbazole **22**, 9-methylcarbazole **23**, and 9-ethylcarbazole **24** were used as electron donors in the reduction of diphenyl sulfoxide **1**. Photolyses with the carbazoles were carried out using the broad band black light bulbs (emission centered at 350 nm) in the Rayonet mini-photoreactors unless otherwise noted. This insured that only the carbazoles absorbed the light. All three of the carbazoles had sufficient extinction coefficients of at least 3000 $M^{-1}cm^{-1}$ at 340 nm. All solutions, unless otherwise noted, were composed of sulfoxide **1** (10 mM), carbazole **22 – 24** (10 mM), and dodecane (5.0 mM) as an internal standard in a solvent that will be noted. They were analyzed by GC.

**Qualitative results with carbazole systems**

The first experiments were conducted in methanol. It was found qualitatively that 9-methylcarbazole **23** produced the best yield of sulfide, but that carbazoles **22** and **24** were similar. It was found that in acetonitrile that only the parent carbazole **22** produced any sulfide. Since carbazoles **23** and **24** do not contain an exchangeable proton and methanol is not present for a proton source, this result may indicate the need of a proton source in the reduction process.

The wavelength of light was varied. Two samples of carbazole **22**, diphenyl sulfide **1**, and dodecane were prepared in methanol. One sample was placed in a photoreactor containing white light bulbs (300 nm) and the other sample was place in a photoreactor containing blacklight bulbs (350 nm). It was found that higher yield of sulfide came from the photolyses at 350 nm and after three hours the sulfoxide **1** irradiated at 300 nm started to decompose.

**Quantitative results with carbazoles systems**

To test sulfide isolation possibilities, reactions were run and diphenyl sulfide was isolated by preparatory thin layer chromatography (TLC). Three solutions of diphenyl sulfoxide **1** (20 mM) in methanol with each the three carbazoles **22**, **23**, and **24** (20 mM) were prepared and argon flushed (25 min.). Each of the samples were photolyzed until the GC trace showed no sulfoxide remaining (generally about 8 h for 50 mL of solution). After the photoreaction, each solution was concentrated to dryness and then each sample dissolved in a minimal amount of methylene chloride. Each sample was then subjected to preparatory TLC (hexanes/ethyl acetate (19/1) mixtures). Carbazole **23**

produced the best yields of diphenyl sulfide (ranged from 40 – 67% yield in three separate experiments). The best yields of sulfide are presented in Table 14

**Table 14.** Isolated yields of diphenyl sulfide **3** from preparatory TLC.

| Carbazole | Percent Yield of Sulfide |
|---|---|
| **22** | 49 |
| **23** | 67 |
| **24** | 63 |

Quantum yields for diphenyl sulfide apperance with N-methyl carbazole **23** as electron donor were determined. Samples containing **1** (10 mM), **23** (10 mM), and dodecane (5.0 mM) in methanol were prepared. The averaged quantum yields for appearance of sulfide from two duplicated runs are shown in Table 15. All quantum yields were determined at less than 10% conversion of sulfoxide. Azoxybenzene was used as an actinometer and photolysis was carried out at 313 nm.

To investigate the effect of the carbazole sensitizer acting as catalysis, a solution with a large amount of sulfoxide **1** (200 mM) with carbazole **23** (20 mM) in methanol was investigated. The solution contained a dodecane (5 mM) as the internal standard. Sulfide could be produced in abundance greater than the sensitizer. Additionally, quantum yields for this solution determined (Table 15). Interestingly, the quantum yield is higher than with lower sulfoxide concentration.

**Table 15.** Quantum yield of the appearance of diphenyl sulfide **3** with N-methyl carbazole **23** as electron donor

| Quantum yield of appearance of sulfide[a] | Quantum yield of appearance of sulfide[a] |
|---|---|
| 10 mM **1** / 10 mM **23** | 200 mM **1** / 20 mM **23** |
| 0.38 | 0.95 |

[a]Estimated error limits of quantum yields are 20 % and values are from the average of two duplicate runs.

**Quenching of carbazoles excited states with sulfoxides**

Given that concentration changes in such a high concentration range affected the quantum yield, it was plausible that a short-lived intermediate, namely the carbazole singlet, was involved. Singlet quenching rate constants were determined by single photon counting experiments. Diphenyl

sulfoxide **1** and DBTO were found to quench the singlet excited state of 9-Methylcarbazole near the diffusion control limit.

Transient absorption experiments to examine the triplet quenching of carbazoles were attempted. Unfortunately, they were rather ambiguous due to overlapping signals and the competition between triplet formation and photoionization.

Utilizing the N-methyl carbazole **23** ($E_T$ = 70 kcal/mol) as the sensitizer and diphenyl sulfoxide **1**, the effect on sulfide yield with a triplet quencher present, isoprene ($E_T$ = 60 kcal/mol) was evaulated. Solutions of varying concentrations of isoprene (0 – 10 mM) with **23** (2 mM), **1** (2 mM) and dodecane (0.5 mM) in methanol were constructed. The solutions were cooled to 0 °C to help prevent isoprene evaporation during argon flushing (20 min.). The solutions were placed in a carousel then photolyzed to less than 20% conversion (about 10 min. with eight 350 nm blacklight bulbs). Upon Stern-Volmer treatment of the data, all data was within 10% scatter of the standard (*i.e.* no isoprene present). This result provided that there was no effect on sulfide yield with the triplet quencher present.

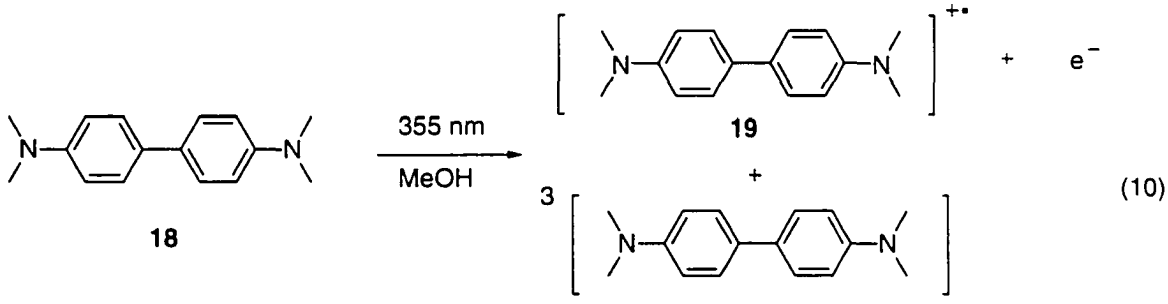
**Sulfoxides resistant to reduction with carbazole systems**

Other sulfoxides that were resistant to reduction were dibenzyl sulfoxide **14** and tetramethylenesulfoxide **25**. Separate solutions of the above sulfoxides (10 mM) and N-methyl-carbazole **23** (10 mM) were prepared. Utilizing dodecane as the internal standard, each solution was photolyzed for over 3 h and no production of sulfide ever became apparent for either **14** or **25**. Sulfoxide **25** was resistant to any chemistry, whereas sulfoxide **14** began to decompose by other pathways.

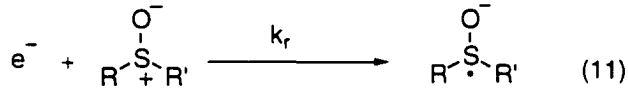
**Quenching of solvated electrons**

The reaction rates of quenching a solvated electron by various sulfoxides were also investigated. Alexandre Darmanyan's work produced solvated electrons through laser flash photolysis of tetramethylbenzidine **18** at 355 nm. After excitation this compound is known to undergo two pathways, as shown in equation 10 and previously by Alkaitis.[17] The pathway of interest involves the production of the radical cation of tetramethylbenzidine **19** and a solvated electron. The solvated

electron transient was quenched by the addition of sulfoxides. Sulfoxides are believed to interact with electrons according to the reaction seen in equation 11.[18-20]




(10)




(11)

The sulfoxide radical anion was not explicitly observed, but this may be due to a short lifetime or a low extinction coefficient. It has been reported that the extinction coefficient for the maximum absorption of the radical anion of dimethyl sulfoxide is small.[20] Darmanyan determined the reaction rates of various sulfoxides with solvated electrons; these data are listed in Table 16.[21]

**Table 16.** Rates of quenching of a solvated electron by various sulfoxides.

| Compound | $k_r$ ($10^9$ $M^{-1}$ $s^{-1}$) |
|---|---|
| Dibenzothiophene oxide | 9.5 |
| Phenyl sulfoxide | 9.1 |
| *p*-Chlorophenyl sulfoxide | 7.6 |
| *p*-Bromophenyl sulfoxide | 7.2 |
| *p*-Methoxyphenyl sulfoxide | 4.7 |
| *p*-Methoxyphenyl methyl sulfoxide | 2.4 |
| Benzyl Sulfoxide | 2.0 |
| Dimethyl Sulfoxide | 0.012 |

**Micellanous electron donors**

Several other electron donors were attempted to reduce diphenyl sulfoxide **1** in methanol. Triethyl amine, trimethyl phosphite, di-*n*-butylsulfide, triphenyl phosphine, and triethyl phosphine were all used as electron donors. Only the two phosphines produced any sulfide.

**Phosphines as electron donors**

A solution of triethyl phosphine (10 mM), sulfoxide 1 (1.0 mM), and dodecane (0.56 mM) in methanol was prepared (Caution using triethyl phosphine; it oxidizes in air very rapidly!). The triethyl phosphine used in this experiment was transferred, in a glove box, to an argon filled vial that was sealed with a septum. Then the triethyl phosphine was added via syringe to a volumetric flask containing methanol, preflushed with argon. This solution was transferred to a septum sealed quartz test tube and further flushed with argon for 20 minutes.

The photolysis of the above solution was carried out using 254 nm light (2 of 8 bulbs in the mini-Rayonets). The reaction only worked marginally in producing diphenyl sulfide. At 90% conversion of **1** only a 30% yield of sulfide was produced. The phosphine oxide was observed in GC runs, but was probably an artifact as it did not grow in.

A solution was prepared with the same concentrations as above, except using triphenyl phosphine (recrystallized twice from hexanes) as the electron donor. The reaction produced less than 10% diphenyl sulfide at 90% conversion of starting material. It should be noted that at 254 nm most of the light was absorbed by triphenyl phosphine and not the sulfoxide.

## Discussion

Photolysis of compound **11** at 300 nm with sodium methoxide has shown an increase in the production of the corresponding sulfide. These results are in good agreement with the findings of Kropp.[14] This experiment also presented another interesting result. By qualitative examination, the production of **13** does not appear to be produced in a 1:1 stoichiometry with sodium methoxide.

This deviation from 1:1 stoichiometry is evident in the 1 mM sodium methoxide experiment in Table 1. A yield on the order of 30-40% is regularly observed. This is expected to be much lower if a 1:1 stoichiometry exists. This implies that the methoxide anion is being reproduced within the reaction. The subsequent large scale photolysis of **1** confirms that methoxide is not being consumed

in the reaction. This shows that the stoichiometry is not 1:1 in respect to sulfide production and the concentration of sodium methoxide. Photolysis of compound **1** at 300 nm in the presence of base showed that an alpha hydrogen is not required for the reaction to occur. In fact, compound **1** may be reduced more efficiently than **11**.

To examine if the solvent was being oxidized, the system of *tert*-butyl alcohol and sodium *tert*-butoxide was examined. As explained previously, *tert*-butyl alcohol should be more difficult to oxidize than methanol if electron transfer occurs because the butoxyl radical does not have an easily lost hydrogen atom. Under such conditions, it is expected that a return to starting materials would be more likely than with methanol oxidation. Thus a decrease in sulfide production should result. Although the reaction was not completely quenched, the production of sulfide was indeed decreased. From this experiment it was shown that a large excess of sodium *tert*-butoxide does not affect the reaction as much as a large excess of sodium methoxide, as shown in previous experiments.

Addition of methanol to the solution or the use of ether instead of water increases the efficiency of the sulfide formation again (Figures 1 and 2). This increased yield in the presence of ether could arise from the ether acting as the species that is eventually oxidized instead of *tert*-butyl alcohol, perhaps by hydrogen atom abstraction. This ability of ether to be oxidized by hydrogen abstraction within the reaction would explain why added methanol had no effect. However, to this point no definite proof has been presented to explain this phenomenon.

It should be noted that there is some ambiguity in the results examining halide anions being applied to the reduction reaction. It is known that halogens oxidize sulfides to sulfoxides in aqueous solutions,[22] it should therefore be noted that these experiments may not have accounted for the re-oxidation of the sulfide to sulfoxide.

Experiments at 254 nm (Figure 3) showed that the yield of sulfide is similar at low conversion for solutions containing 100 and 200 mM sodium methoxide. More intriguing is the observed induction period at low conversion of sulfoxide. Initially it was proposed that residual oxygen could be responsible for the induction period. This was proposed because previous qualitative experiments showed that the presence of oxygen may result in complete quenching or a severe reduction in the sulfide production. Experiments utilizing the FPT degassing technique showed that the induction

period was still present. However, the induction period appears not to be related to residual oxygen within the sample. Investigation of possible impurities on the induction period, purification of diphenyl sulfoxide and the use of freshly prepared sodium methoxide did not reduce the induction period. There is still this ambiguity in what causes the induction period. However, the methoxide system is the set of conditions in which the induction period was observed.

Substantial concentrations of oxygen in the sample severely retard the photoassisted reduction reaction. When methoxide is not present within the sample, oxygen saturation produces a different ratio of products when compared to an argon degassed sample, but does not quench the production of sulfide. This leads to the conclusion that the oxygen is quenching a process that is unique to the photoassisted mechanism.

The quantum yields of **1** at 254 nm indicate that the largest excess of sodium methoxide leads to the largest quantum yield of sulfide, presumably because of an inefficient quenching event. The increase in efficiency that is observed at higher concentrations of sodium methoxide could also be due to the methoxide anion absorbing greater amounts of light and photoionizing. This would produce more solvated electrons to be used in the reaction. By the same token, the increase in base concentration increased the efficiency of the reaction perhaps by enabling the excited state of the sulfoxide to be more efficiently quenched by methoxide anion. Therefore the observed rate of increase does not differentiate between the sulfoxide or the methoxide anion from being the key component that is absorbing light.

The experiment that examined the photolysis comparing the presence of aniline **16** and pyridine **17** is very interesting. Since the $pK_B$ values for these two compounds are similar, it was expected that they would both deprotonate methanol in relatively equal but small amounts. Thus, if the formation of methoxide anion was responsible for deoxygenation, these systems should show very similar results and low yields. However, aniline effects the reduction reaction but pyridine does not. This can be explained because aniline is a known electron transfer agent,[23] while pyridine, on the other hand, is not. Therefore the ability of the added base to donate an electron may be important to the success of the reduction reaction. This is consistent with the mechanism involving the photoionization of methoxide anion or electron transfer from hydroxide to $Ph_2SO^{\bullet}$.

Continuing on the subject of electron transfer, Darmanyan suggested that the observed long-lived intermediate resulted from the photoejection of an electron by the methoxide anion. This result led to the realization that sodium methoxide may also be very slightly absorbing light and the production of solvated electrons may be important to the success of the reaction. The photoionization of carbazoles and anilines is also consistent with production of solvated electrons in polar solvents.[24,25]

Further work by Darmanyan has indicated that not only may the production of solvated electrons be important to the reaction, but the rate at which the sulfoxide reacts with them may also be noteworthy. The sulfoxides that were examined in this study, namely compounds **1** and **6** show a nearly diffusion-controlled rate constant reacting with a solvated electron. The compound **14** reacts much slower. This may explain why **14** does not show an observable increase in the production of sulfide. In order to make a more useful correlation to the rate of quenching of solvated electrons, more sulfoxides must be studied.

The experiments photolyzing the aromatic amines **16**, **20**, and **21** in the presence of sulfoxide also suggests more evidence that the production and quenching of solvated electrons may be important to the reduction reaction. These experiments also show that other solvents may be used for the photoassisted reduction although methanol is still the best solvent as shown from quantum yield measurements of the appearance of sulfide **3** (Table 13). The other subtle effect that was looked for with the reduction is the formation of aniline from demethylation of N-methylaniline **20**. The demethylation of **20** could occur from hydrogen abstraction followed by oxidation. No formation of aniline was observed thereby indicating this is not the route of oxidation at least with **20**.

Carbazoles **22**, **23**, and **24** were shown to be very effective as reducing agents in the reduction of **1**. From the isolation experiments, the isolation of sulfide **3** by preparatory TLC indicated that 9-methylcarbazole **23** is the best reducing agent out of the three carbazoles studied. Unlike the aniline case, the only solvent system that was productive for the reduction process with the carbazoles was methanol. Given that, an intriguing result came from the solvent effect study. This result was that in aprotic solvent only the parent carbazole **22** was able to produce any sulfide, thus indicating the need of a proton source for the reduction.

The quantum yield experiments with **23** led to similar yields of sulfide **3** as with the aniline systems when equal molar amounts of electron donor and sulfoxide were used. However, when the carbazole **23** was used in low concentration versus high concentration of sulfoxide, the quantum yield for the appearance of sulfide was very high ($\Phi = 0.95$). Thus a catalytic effect with carbazole **23** must be operating.

The singlet quenching rate constants of carbazole **23** were found to near the diffusion control limit with sulfoxide **1**. Sulfoxide **14**, as with the quenching of the solvated electron, was found to quench the excited with a somewhat slower rate constant. Isoprene, a triplet quencher was found not to impede sulfide formation. Therefore, these quenching experiments lead to data that is consistent with the reduction occurring from the singlet excited state of the carbazole or a solvated electron, but not the triplet state.

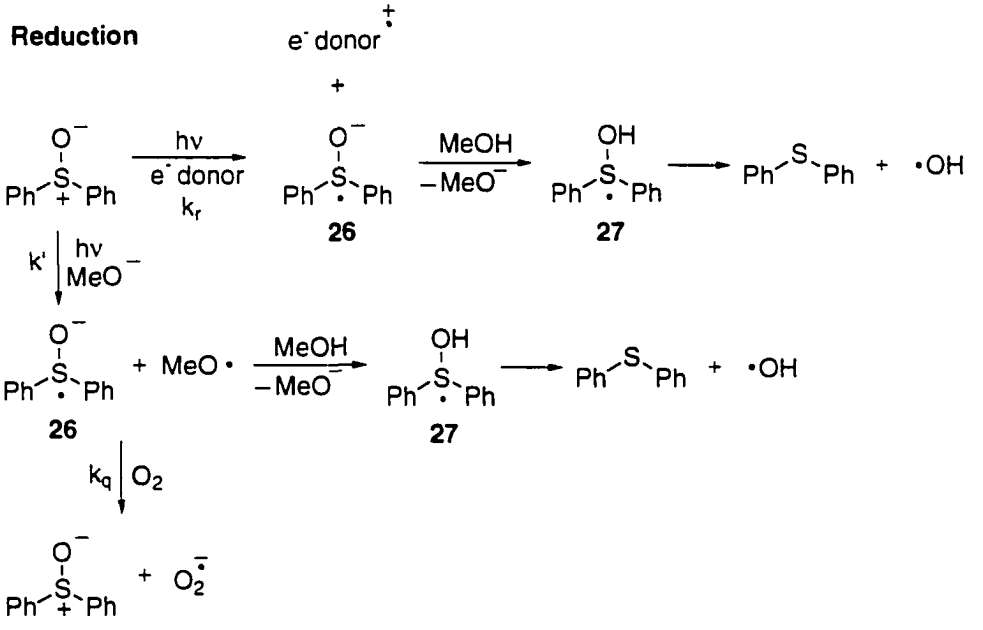
Several other electron donors (triethyl amine, trimethyl phosphite, and di-*n*-butyl sulfide) were tried but evidently they were not efficient enough at donating electron to promote reduction. Only the phosphines were able to promote reduction, with triethyl phosphine being the better than triphenyl phosphine. Comparison of the triethyl phosphine system with the sodium methoxide system produced lower yields of sulfide, qualitatively.

A comparison of the systems studied will be presented here. The carbazoles are the electron donors of choice. The carbazole reaction in the aniline systems other solvents produces sulfide very efficiently and cleanly. The aniline systems also work efficiently in producing sulfide but tend not to be as clean. Sodium methoxide and triethyl phosphine tended not to work as well as the aniline or carbazoles systems. Methanol, a proton source, was found to be the best solvent although worked (Table 13) (e.g. THF produced a quantum yield of sulfide similar to the observed quantum yield of sulfide in methanol.)

A mechanism is proposed for the photoassisted reduction of sulfoxides to sulfides in Figure 8. This mechanism illustrates possible pathways by which oxygen may quench the reaction ($k_q$). It also proposes a possible system for the oxidation of solvent to formaldehyde. This mechanism proposes two similar pathways to obtain the sulfoxide radical anion **26**. One pathway assumes an electron transfer from an electron donor (e.g. aniline or carbazole) to the ground state sulfoxide ($k_r$). After

production of sulfide it is proposed that the electon donor is regenerated by oxidation of the solvent. The other pathway (k') assumes an electron is transferred from methanol to the sulfoxide.

This mechanism also incorporates the hydroxy-sulfuranyl radical **27**, which was proposed by Kropp.[14] Persistent sulfuranyl radicals have been observed by ESR spectroscopy.[26] The observance of a hydroxy-sulfuranyl radical **27** has only been previously supposed.[27] Likewise, the observance of hydroxydimethylsulfuranyl radical **27** has been detected experimentally[28] to be a reversible intermediate with the binding energy of approximately of 10 kcal/mol, in relative aggreement with high level ab initio calculations have argued for the existence of compound **27**.[29] For the purposes of this dissertation it is assumed that formation of compound **27** was achieved followed.




**Possible Oxidation in Methoxide System**

$$\bullet OH + \bullet OMe \longrightarrow [HO\text{-}OMe] \longrightarrow H_2O + CH_2O$$

**Possible Oxidation in Carbazole/Aniline Systems**

$$\bullet OH + MeOH \longrightarrow \bullet CH_2OH + e^- donor^{+\bullet} \longrightarrow e^- donor + CH_2O + H^+$$

**Figure 8.** A proposed mechanism for the photoassisted deoxygenation of sulfoxides to sulfides.

# Conclusions

The dramatic increase in sulfide yield observed by Kropp[14] for the photolysis of sulfoxide **8** in the presence of sodium methoxide has been substantiated by numerous experiments. Data consistant with Kropp's proposed mechanism was presented here. Some factors that influence the success of the reaction include the following: the ability of the added base to produce solvated electrons, the rate at which solvated electrons react with sulfoxide, the ease of which an agent in the reaction solution is oxidized, and the wavelength of the irradiation. Also the presence of oxygen has an adverse effect on the production of sulfide.

Other electron donors were found to be much more efficient at reducing sulfoxides than sodium methoxide. The best electron donors were 9-methyl carbazole and N-methyl aniline. Data consistent with the reduction, utilizing carbazoles, occurring out of the singlet state was presented. The necessities in order for the photo-reduction to occur are a photon, an electron donor, and a proton source.

# Experimental

### General Instrumentation

$^{1}H$ and $^{13}C$ NMR were obtained on a Varian VXR-300 MHz spectrometer. HPLC data were collected with a HP 1050 liquid chromatograph with diode array detector. An ODS Hypersil reverse phase column (5μm, 200 x 2.1 mm, Hewlett Packard) was used. Eluents consisted of an acetonitrile/water gradient. UV spectra were obtained on a Shimadzu UV-2101 PC UV-Vis scanning spectrophotometer. GC data were collected on an HP/5890 series II GC and a Phenomenex Zebron ZB-5 (5% Phenyl Polysiloxane) capillary column (30 m x 0.25 mm ID x 0.25 mm FT) was employed. Lifetimes for the singlet quenching experiments were collected on an Edinburgh Instruments FL-900 single photon counting fluorometer.

### General Methods

Response factors (±10%) for sulfoxides and sulfides were determined against the internal standard p-xylene for HPLC and dodecane for GC. Quantum yields (±20%) were obtained by using

the actinometer azoxybenzene.[15] The inherent error in quantum yield measurements is due to the fluctuation of $I_0$, and also the error associated with the obtainment of a response factor.

**Reagents**

HPLC grade methanol (Fisher Scientific) was used as received. To certified *tert*-butyl alcohol (Fisher Scientific) was added either 1% water or 1% ethyl ether to lower the melting point prior to photolysis. Sodium methoxide (Mallinckrodt) was used as received or as prepared as described in the text. Pyridine **17** (Fisher Scientific), anilines **16**, **20**, and **21** (Aldrich), carbazoles **22** – **24**, *p*-xylene **12** (Aldrich, HPLC grade), and dodecane were used as received. Triethyl amine, trimethyl phosphite, di-*n*-buthyl sulfide were distilled before use. Triethyl phosphine was transferred in a glove box to a septum seal vial under argon. Triphenyl phosphine was recrystallized from hexanes twice before use. Sodium *tert*-butoxide was produced by placing sodium metal (1.9 g) into *tert*-butyl alcohol (20 ml). The mixture was reacted overnight and the solvent was removed by vacuum.

For the flash photoylsis experiments please refer to Troy Teztlaff's thesis.[30]

**Compounds**

The compounds diphenyl sulfoxide **1**, diphenyl sulfide **3**, methyl phenyl sulfoxide **11**, and methyl phenyl sulfide **13** were all purchased from Aldrich and used as received unless otherwise noted. Dibenzothiophene **7** (Acros) and dibenzyl sulfide **14** (Eastman Kodak) were used as received.

**Photolyses**

Two different photolytic systems were utilized in these experiments. The most commonly used was the Southern New England Ultraviolet Rayonet mini-reactor. This reactor had been modified to contain both a fan and a magnetic stirrer. The fan maintained the photoreactor at ambient temperature. The magnetic stirrer guaranteed a uniform solution for photolysis. All reported photolyses were stirred with micro-stir bar at ambient temperature. For the 254 nm photolyses, clear quartz low pressure mercury bulbs at 253.7 nm were utilized. The 300 nm experiments used coated low pressure mercury bulbs with an emission band centered at 300 nm ± 24 nm. The 350 nm experiments used broad band blacklight bulbs with an emission band centered at 350 nm.

The second system employed a 150 W Xe lamp and monochromator from Photon Technologies, Inc. The monochromator was used to select the desired photolysis wavelength, and slit widths allowed for ± 12 nm linear dispersion. For the photolyses in the Rayonet mini-reactor, 12 mm diameter quartz test tubes were used in conjunction with the merry-go-round sample holder to ensure uniform incident irradiation. Photolyses utilizing the monochromator were performed using standard 1 cm quartz cells. Unless otherwise stated, all samples were degassed with Argon for 20 minutes. During photolysis, samples of approximately 0.1 ml were extracted by syringe, neutralized with a saturated ammonium chloride methanol solution, and analyzed by HPLC. Unless otherwise noted, samples contained 10 mM sulfoxide, 1-3 mM p-xylene as internal standard, and varying amounts of sodium methoxide.

Photolyses of carbazole, aniline, and phosphine systems were analayzed by GC with samples (0.1 mL) taken by syringe and then shot directly onto the GC. The carbazole/aniline systems were generally contained 10 mM sulfoxide, 5 mM dodecane as an internal standard, and 10 mM carbazole or aniline, unless otherwised noted in the text. The phosphine systems were run at 2 mM sulfoxide, 2 mM phosphines, and 0.5 mM dodecane as an internal standard.

**Single photon counting measurements.** All luminescence lifetimes were measured at room temperature. Quenching rate constants were by measurement of the fluorescence lifetime of 9-methylcarbazole as a function of diphenyl sulfoxide concentration (excitation wavelength = 353 nm, emission wavelength = 396) . Samples were prepared in methanol with 1 mM carbazole and 0 – 2.5 mM sulfoxide and purged with argon for 10 minutes.

**Synthesis**

**Dibenzothiophene oxide 6** was prepared by the method of Davis[31] in 65% yield.

**Phenoxathiin oxide 14.** Phenoxathiin oxide was obtained in 78% yield by oxidation of Phenoxathiin (Aldrich) by $Bu_4N^+IO_4^-$ and catalytic (5,10,15,20-tetraphenylporphine) iron (III) chloride.[32,33]

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# GENERAL CONCLUSIONS

The mechanism of the Ei reaction for sulfoxides, sulfinyl derivatives, and sulfones was characterized. A computation study of simple sulfoxides allowed description of the excited potentials for the mechanism of photostereomutation. The bimolecular photo-reduction mechanism of aryl sulfoxides was thoroughly investigated.

The Ei reaction for sulfoxides, sulfinyl derivatives, and sulfones was investigated with gas-phase kinetics and computations. Experimental activation barriers were found to compare closely with computed activation barriers, once an adequate basis set was used. The activation barriers for the Ei reaction of sulfoxides were found to be fairly insensitive to substituent effects. Exceptions to this insensitivity were found when the β-proton was acidic, when the olefin being form was going into conjugation, and when there was steric crowding. The sulfinate ester was new molecule found to undergo the Ei reaction. The activation barrier for the thiosulfinate was found to be much lower than the sulfinate esters and sulfinamides. From calculation access to several molecule's elimination energetics, unsuited for experimental study via the SFR, were investigated computationally. Simple alkyl sulfones were characterized to under the Ei reaction through substituent effects, isotope effects, and computations.

From the excited state computational study on $H_2SO$ and DMSO, photostereomutation was found to be a viable pathway. This study allowed access to excited state geometries of sulfoxides that have never before been observed. One of these geometries, namely the T-shape geometry can be accessed without barrier from the vertically excited sulfoxide. This provided evidence in support for photoinversion without C-S cleavage out of the lowest lying singlet state. From the vertical triplet geometry, inversion was found to compete with the C-S cleavage pathway.

The bimolecular photo-reduction of aryl sulfoxides to sulfides was found to support the previous mechanism suggested by Kropp and colleagues. Several electron donors were found to reduce the sulfoxide moiety efficiently. It was shown that the light could be directed in either the sulfoxide or the electon donor to achieve reduction. Carbazoles and anilines provided best yields of

sulfides. From the carbazole quenching experiments, the reduction was suggested to occur out of the singlet manifold or from a solvated electron, but not the triple manifold.

This dissertation has added meaningful data to better understand a variety of mechanisms that occur with various sulfur oxidation states. It is hope that the reader understands the importance that computational chemistry plays in deciphering experimental complexities. The use of many different computational theories allowed access to many different chemistry problems. With computers finally coming of age, larger chemical problems can now be attacked. Since the quantum chemical codes require both large memory allotment and hard disk space, chemical problems that were only mere dreams of chemists a few years ago are becoming reality.

# APPENDIX 1

## KINETIC PLOTS FOR SULFOXIDES, DERIVATIVES AND SULFONES

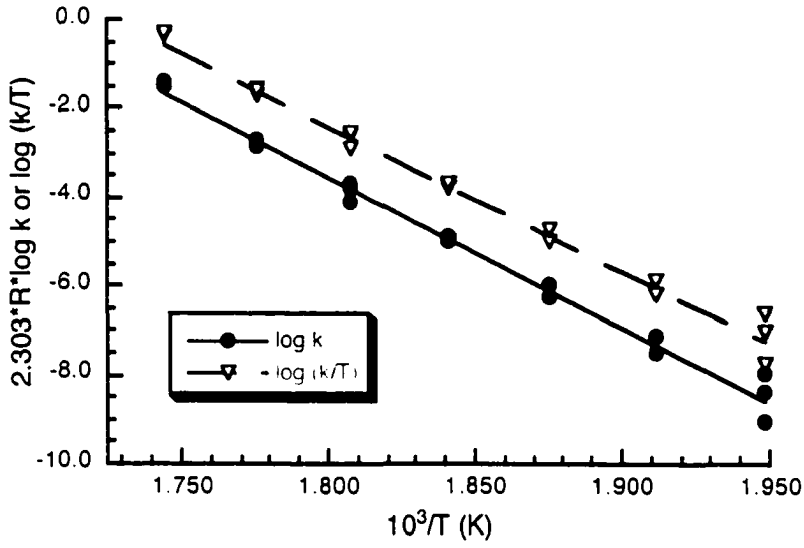



**Figure 1.** Arrhenius and Eyring plots of Methyl 3-phenylpropyl sulfoxide (240° – 300°C).

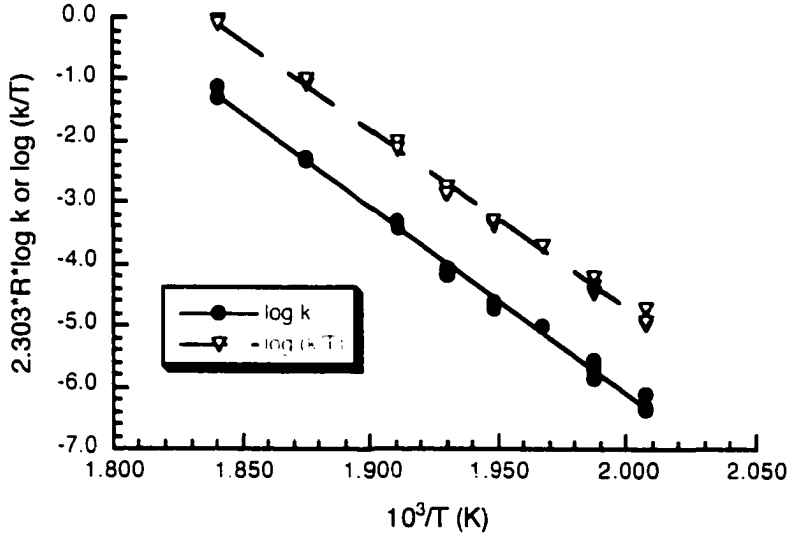



**Figure 2.** Arrhenius and Eyring plots of Vinyl 3-phenylpropyl sulfoxide (225° – 270°C).

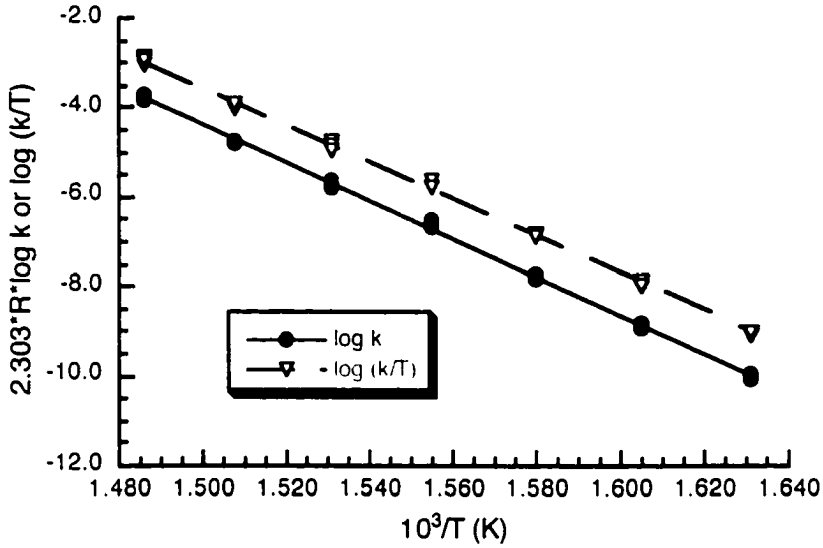



**Figure 3.** Arrhenius and Eyring plots of Methyl vinyl sulfoxide (340° – 400°C).

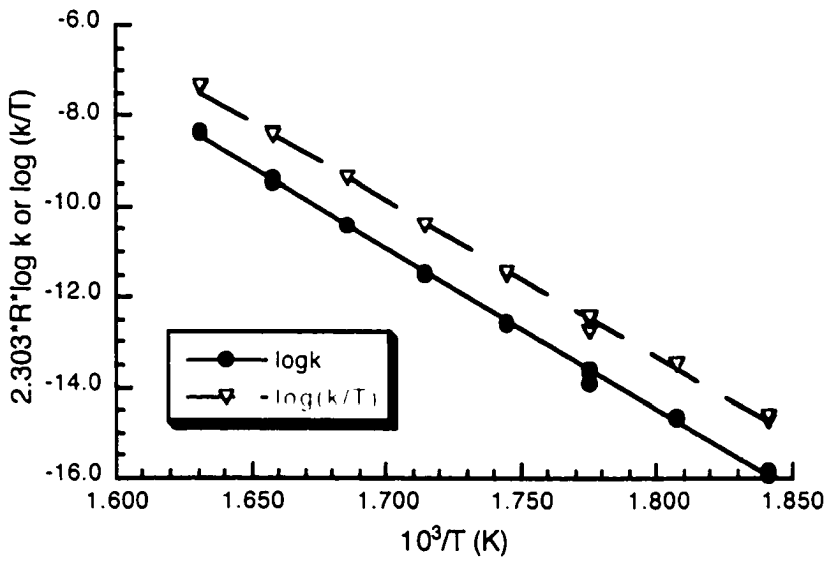



**Figure 4.** Arrhenius and Eyring plots of 3-Phenylpropyl methanesulfinate (270° – 340°C).

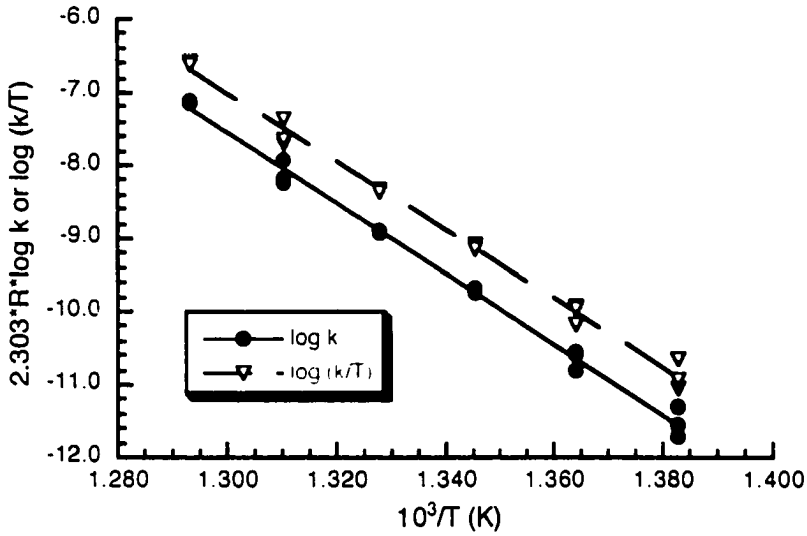



**Figure 5.** Arrhenius and Eyring plots of Methyl 3-phenylpropyl sulfone (450° – 500°C).

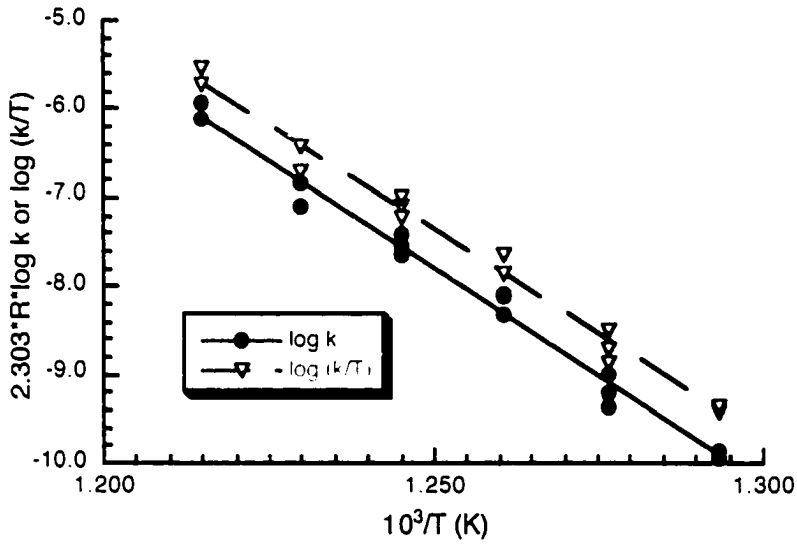



**Figure 6.** Arrhenius and Eyring plots of Phenyl 3-phenylpropyl sulfone (500° – 550°C).

# APPENDIX 2

## GEOMETRIES OF SULFOXIDES, SULFINYL DERIVATIVES, AND TRANSITION STATES

Atoms are color coded:

Red = oxygen
Gray = carbon
White = hydrogen
Yellow = sulfur
Green = fluorine
Blue = nitrogen

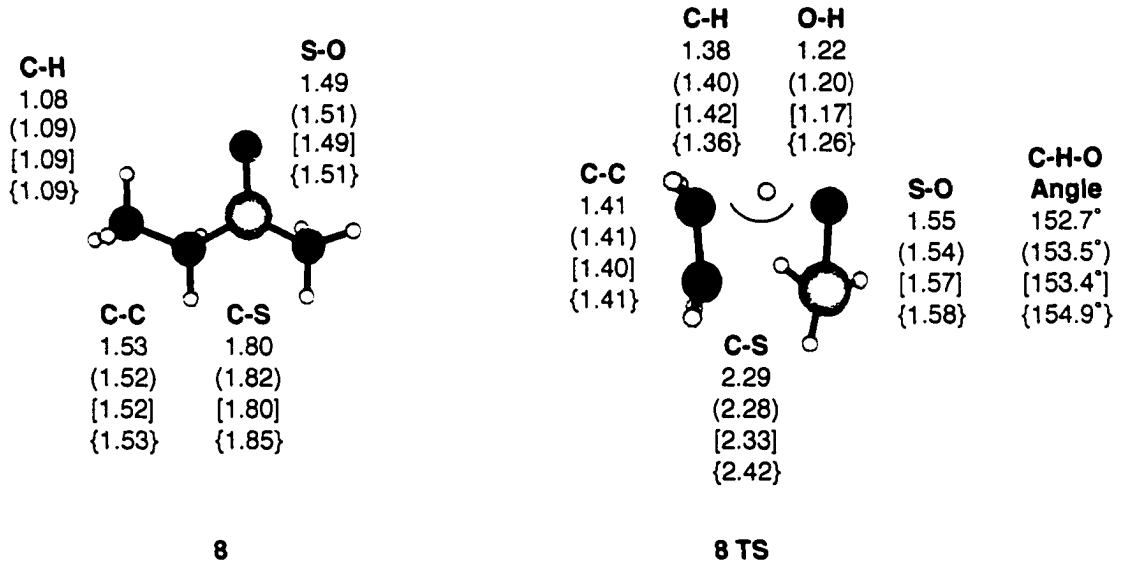



**Figure 1**. Geometry of Ethyl Methyl Sulfoxide, **8**, and its transition state, **8 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), (MP2/6-31G(d,p)), [MP2/6-311+G(3df,2p)], and {Becke3LYP/6-31G(d,p)}, respectively.

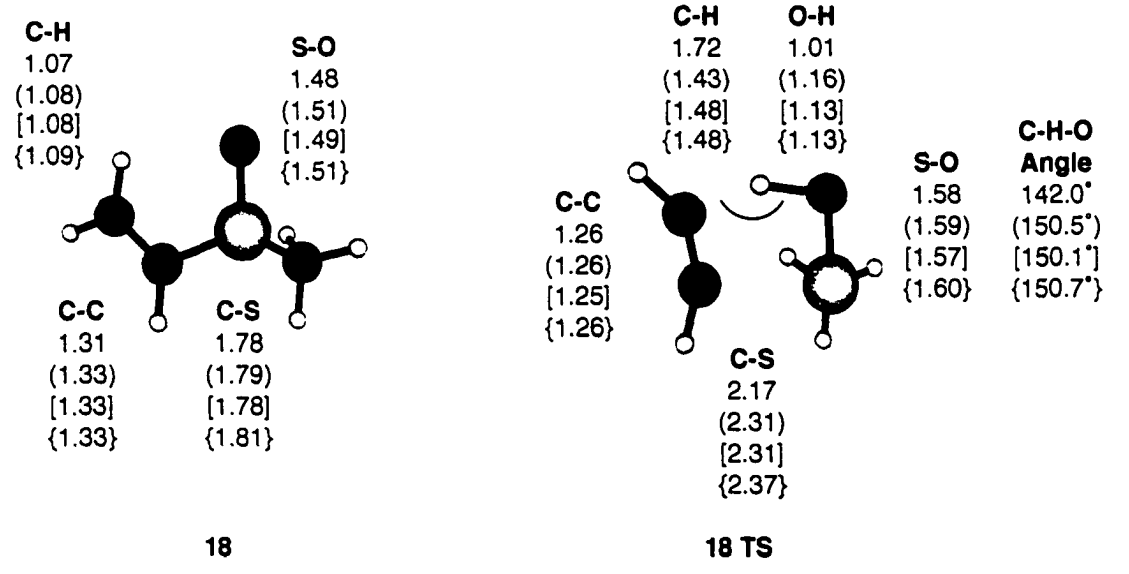



**Figure 2**. Geometry of Methyl Vinyl Sulfoxide, **18**, and its transition state, **18 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), (MP2/6-31G(d,p)), [MP2/6-311+G(3df,2p)], and {Becke3LYP/6-31G(d,p)}, respectively.

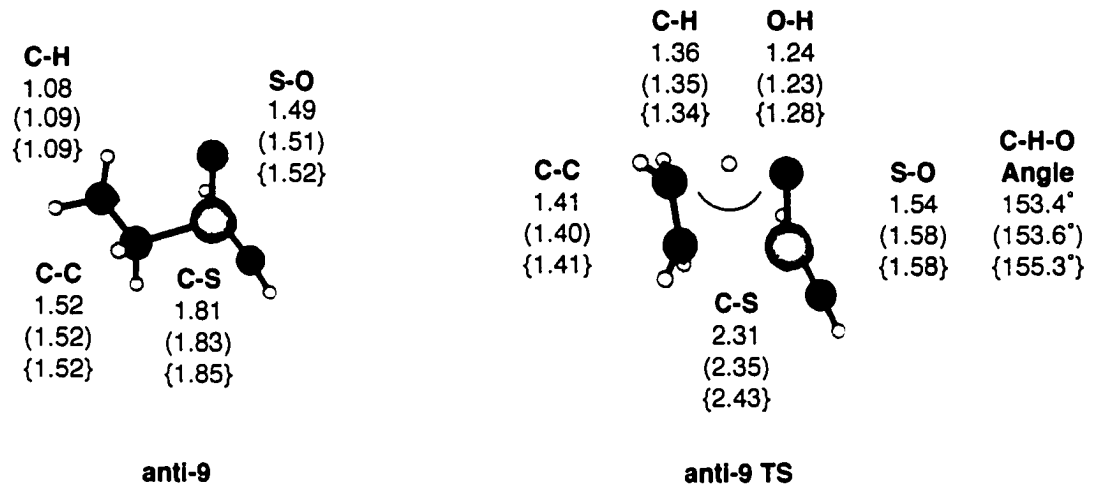



**Figure 3**. Geometry of Ethyl Vinyl Sulfoxide, **anti-9**, and its transition state, **anti-9 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), (MP2/6-31G(d,p)), and {Becke3LYP/6-31G(d,p)}, respectively.

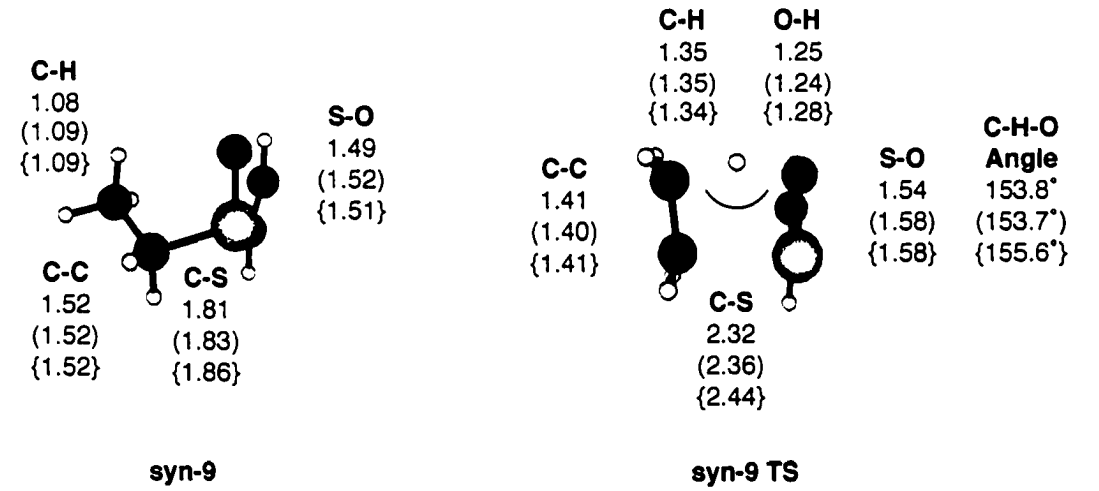



**Figure 4**. Geometry of Ethyl Vinyl Sulfoxide, **syn-9**, and its transition state, **syn-9 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), (MP2/6-31G(d,p)), and {Becke3LYP/6-31G(d,p)}, respectively.

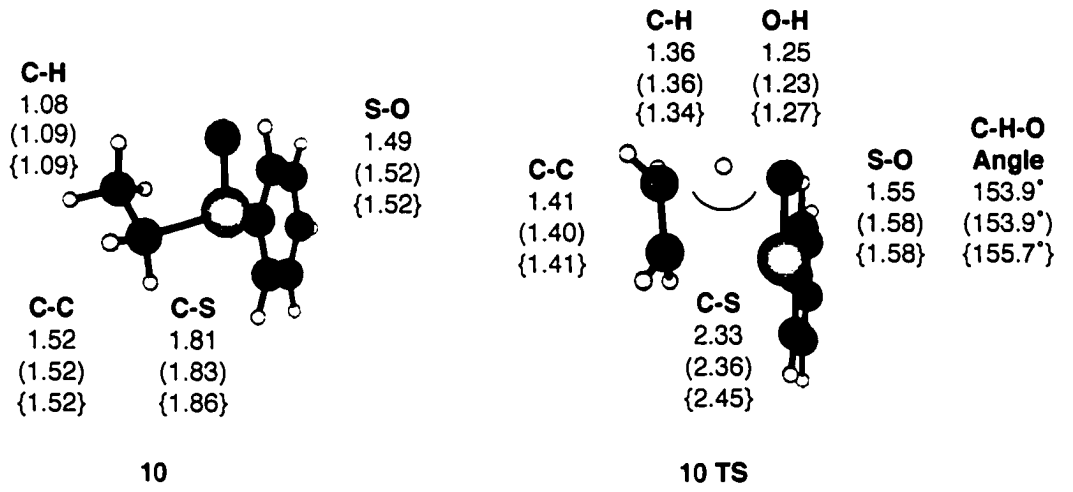



**Figure 5**. Geometry of Ethyl Phenyl Sulfoxide, **10**, and its transition state, **10 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), (MP2/6-31G(d,p)), and {Becke3LYP/6-31G(d,p)}, respectively.

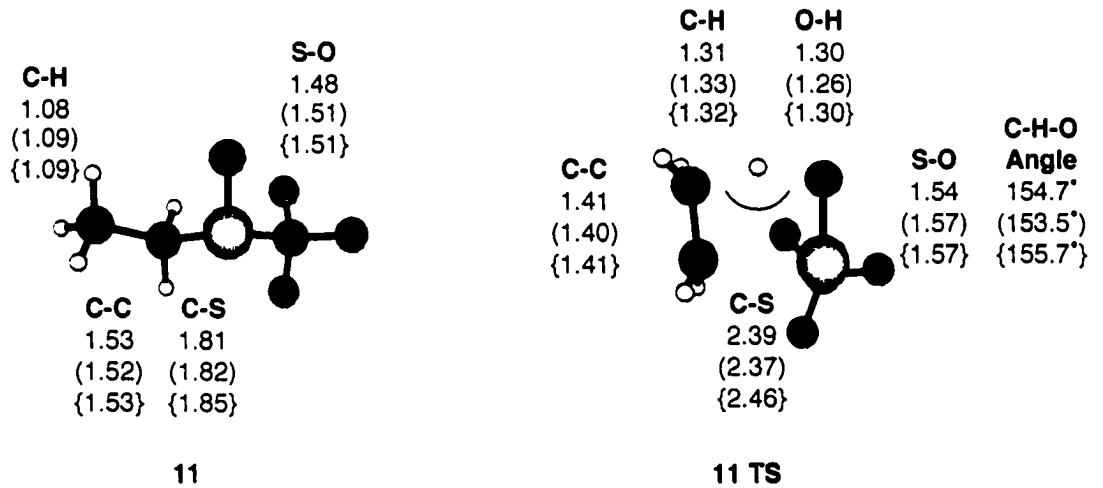
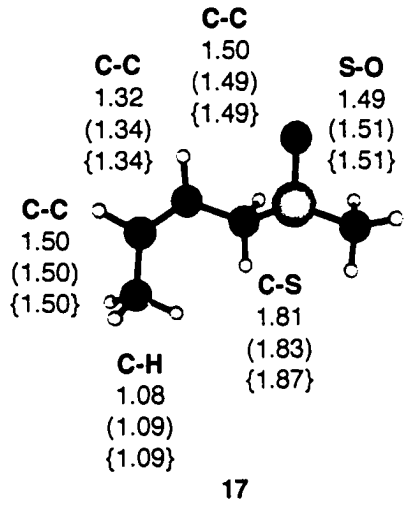



**Figure 6**. Geometry of Ethyl Trifluoromethyl Sulfoxide, **11**, and its transition state, **11 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), (MP2/6-31G(d,p)), and {Becke3LYP/6-31G(d,p)}, respectively.



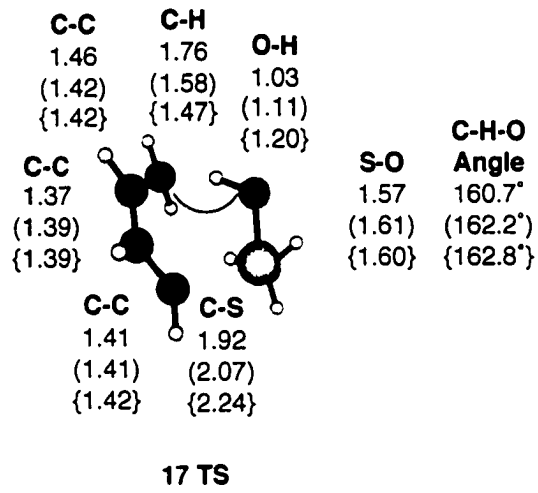
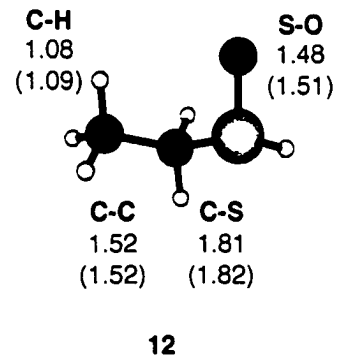




**Figure 7**. Geometry of (Z)-2-Butenyl Methyl Sulfoxide, **17**, and its transition state, **17 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), (MP2/6-31G(d,p)), and {Becke3LYP/6-31G(d,p)}, respectively.



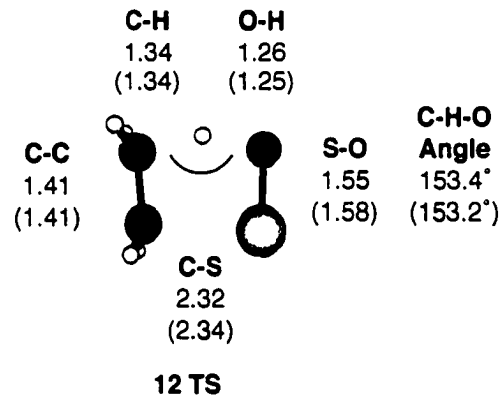




**Figure 8**. Geometry of Ethyl Mercaptan S-Oxide, **12**, and its transition state, **12 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

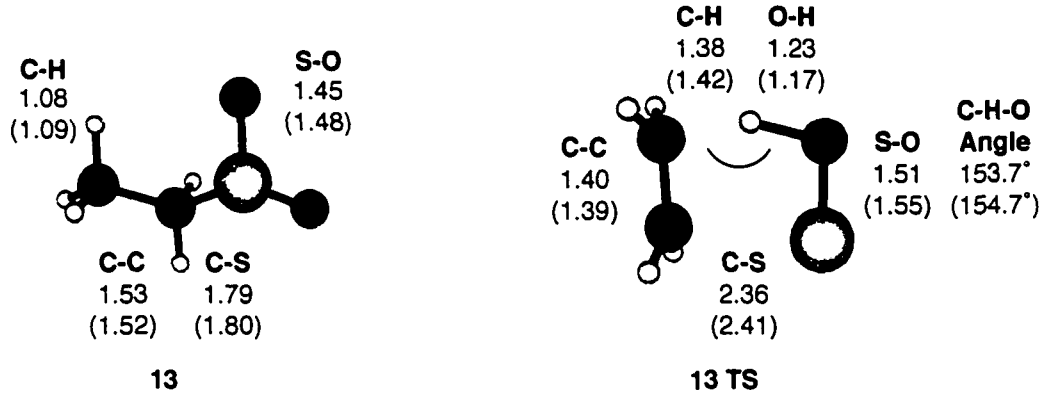



**Figure 9**. Geometry of Ethyl Fluoro Sulfoxide, **13**, and its transition state, **13 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

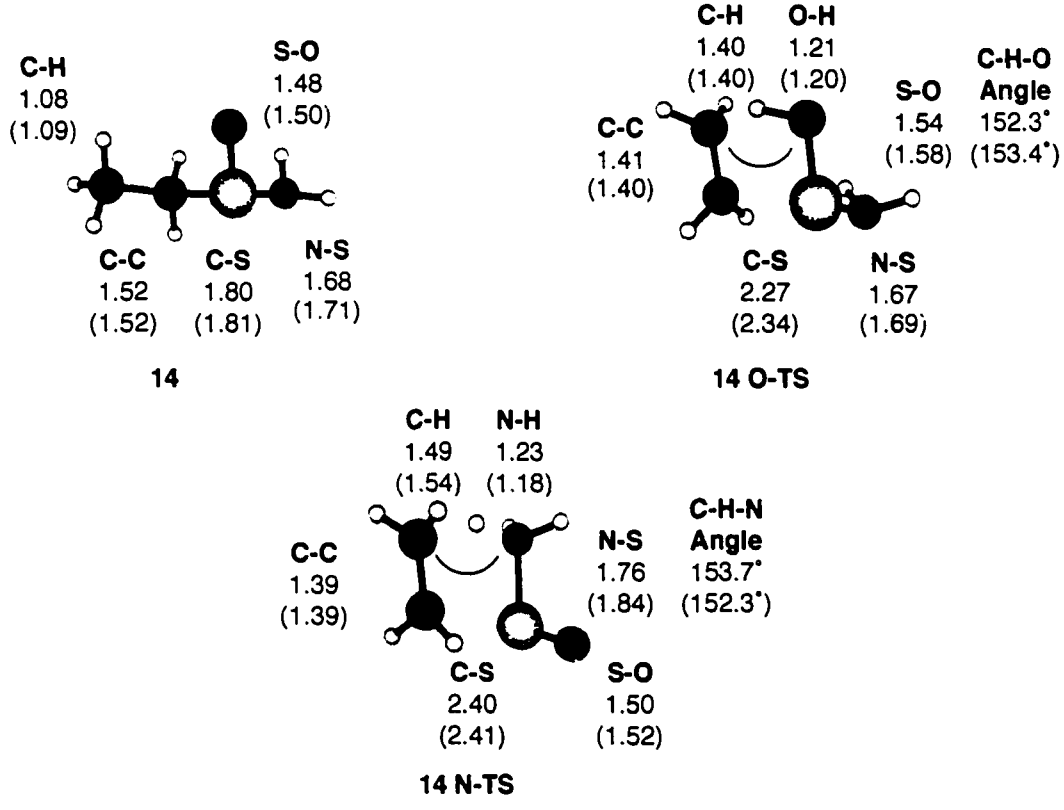



**Figure 10**. Geometry of Ethane Sulfinamide, **14**, and its transition states, **14 O-TS** and **14 N-TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

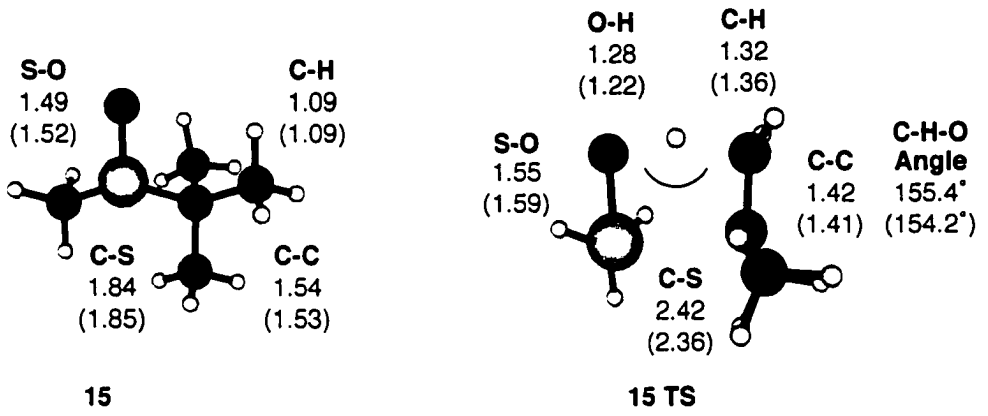



**Figure 11**. Geometry of t-Butyl Methyl Sulfoxide, **15**, and its transition state, **15 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

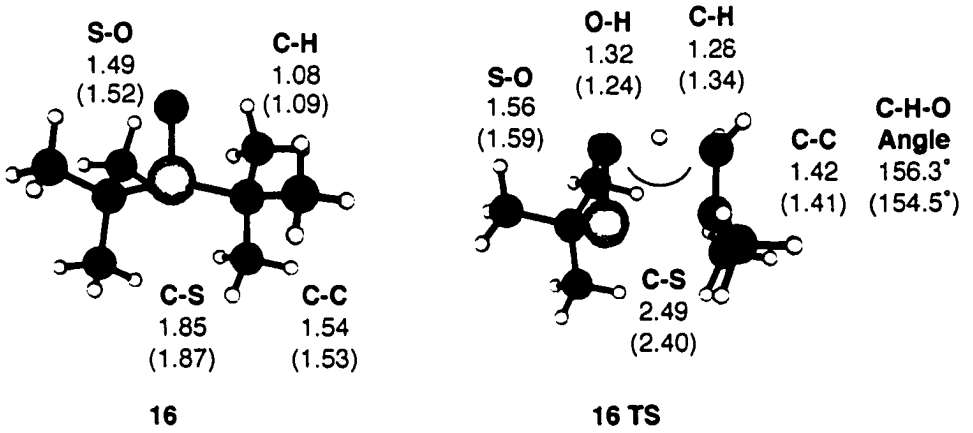



**Figure 12**. Geometry of Di-t-Butyl Sulfoxide, **16**, and its transition state, **16 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

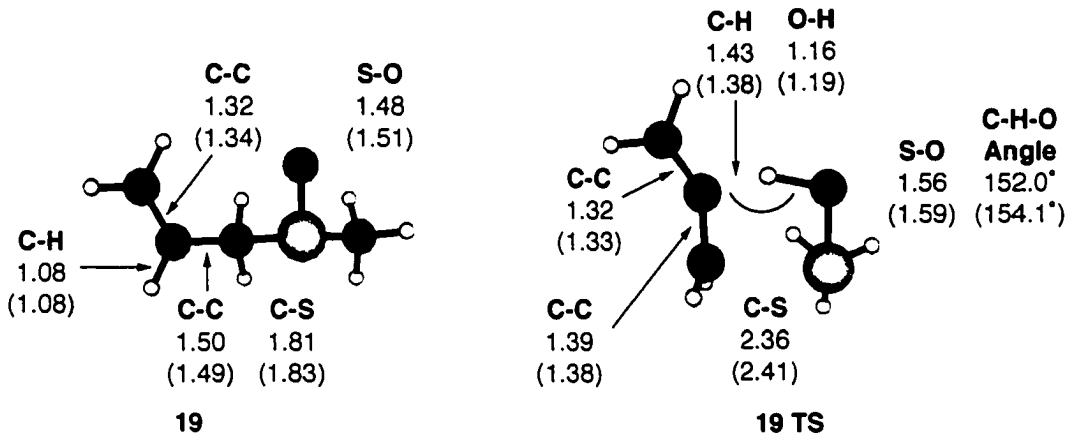



**Figure 13**. Geometry of Allyl Methyl Sulfoxide, **19**, and its transition state, **19 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

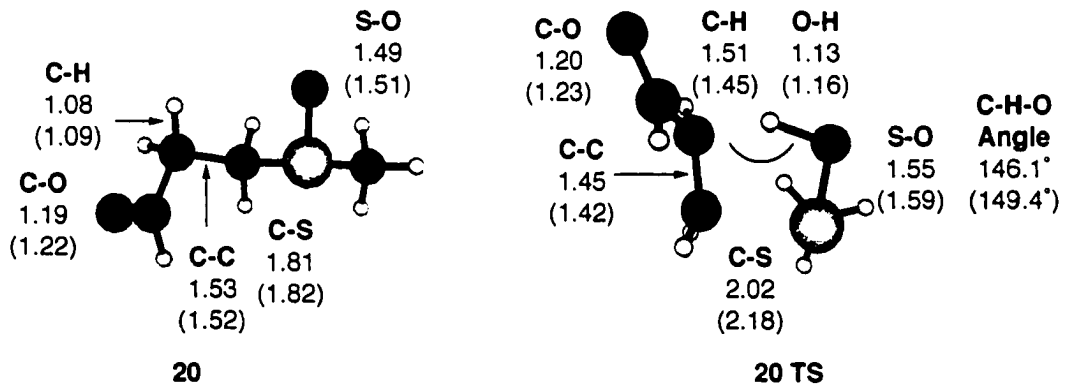



**Figure 14**. Geometry of 3-Methanesulfinyl-1-propanal, **20**, and its transition state, **20 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

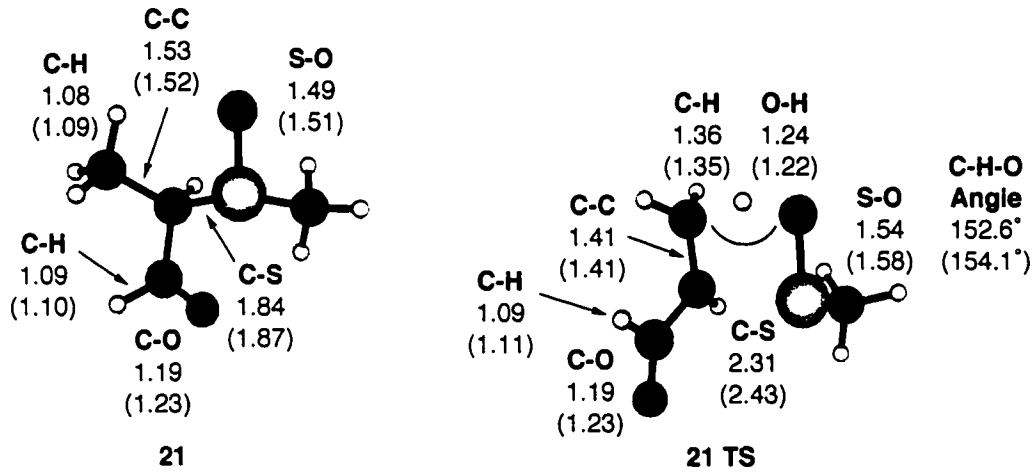



**Figure 15**. Geometry of 2-Methanesulfinyl-1-propanal, **21**, and its transition state, **21 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

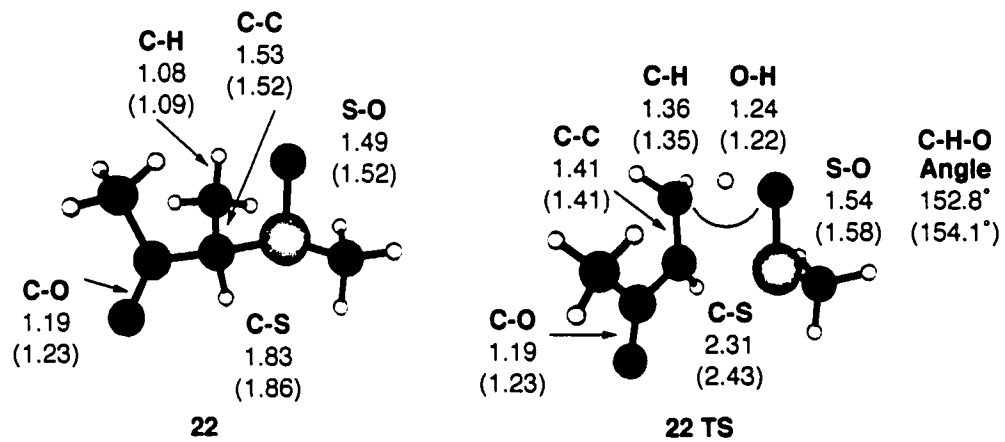



**Figure 16**. Geometry of 3-Methanesulfinyl-2-butanone, **22**, and its transition state, **22 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

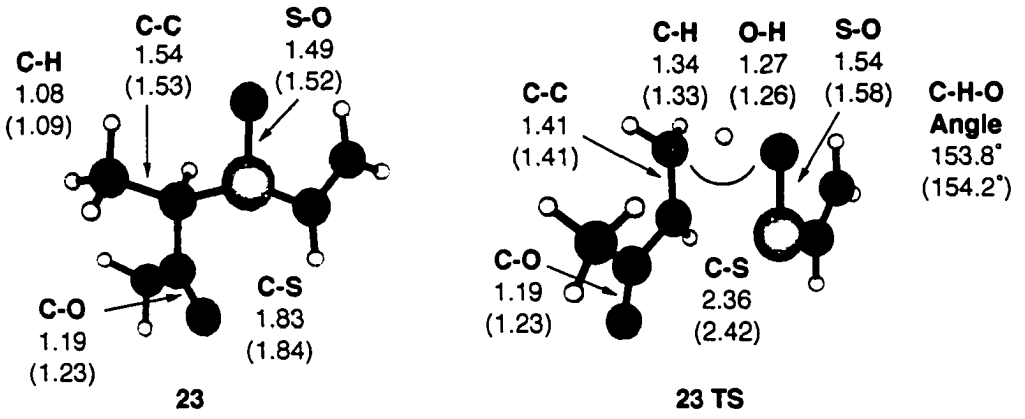



**Figure 17**. Geometry of 3-Ethenesulfinyl-2-butanone, **23**, and its transition state, **23 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

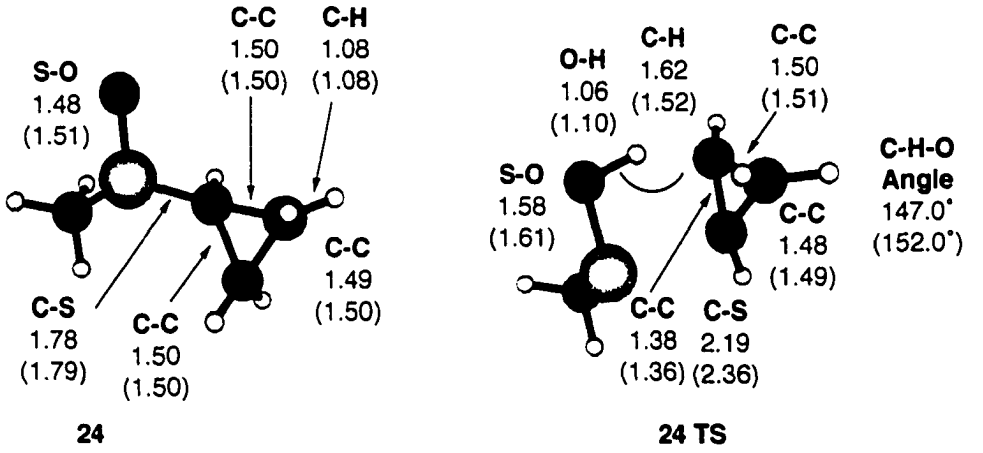



**Figure 18**. Geometry of Cyclopropyl Methyl Sulfoxide, **24**, and its transition state, **24 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

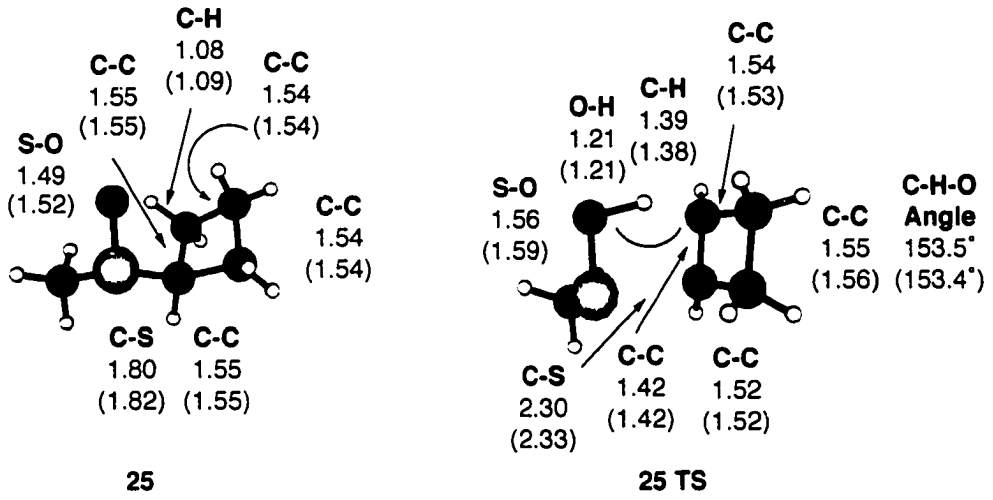



**Figure 19**. Geometry of Cyclobutyl Methyl Sulfoxide, **25**, and its transition state, **25 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

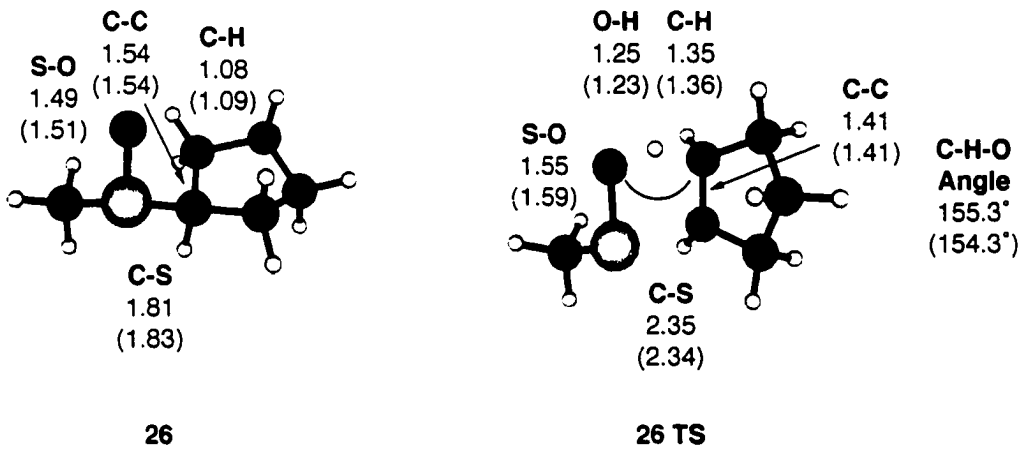



**Figure 20**. Geometry of Cyclopentyl Methyl Sulfoxide, **26**, and its transition state, **26 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

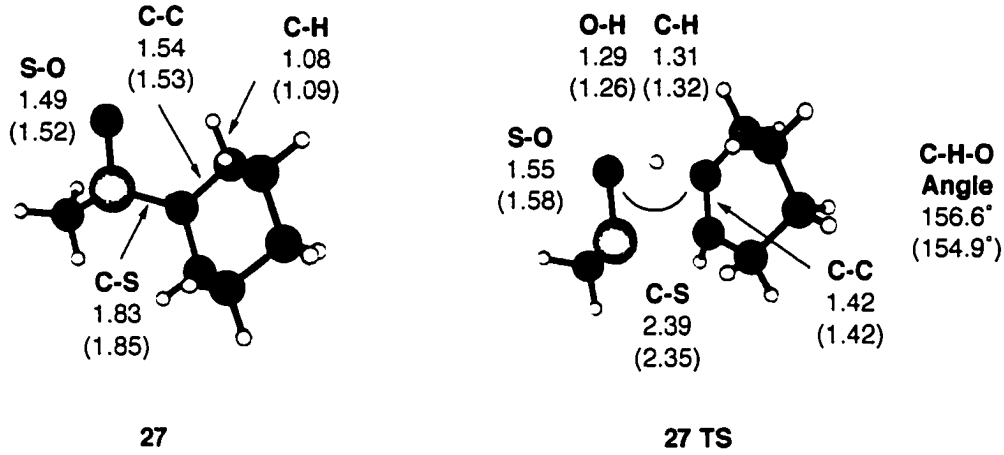



**Figure 21**. Geometry of Cyclohexyl Methyl Sulfoxide, **27**, and its transition state, **27 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

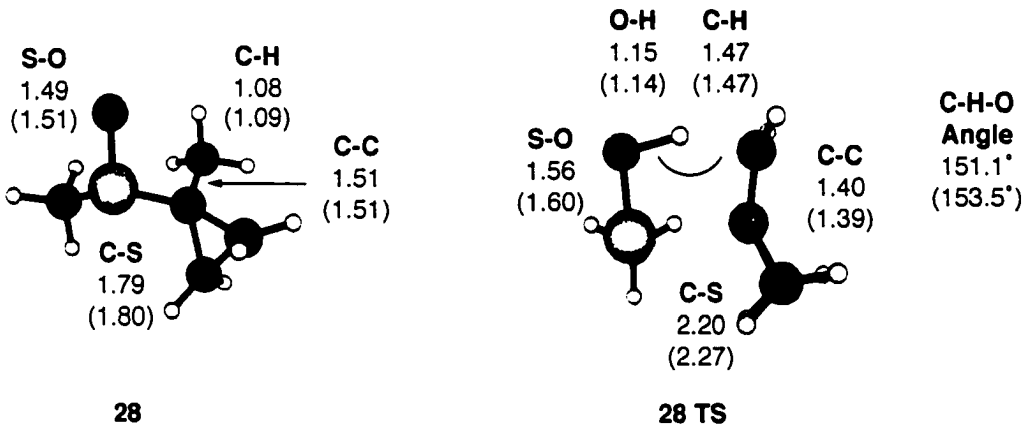



**Figure 22**. Geometry of 1-Methylcyclopropyl Methyl Sulfoxide, **28**, and its transition state, **28 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

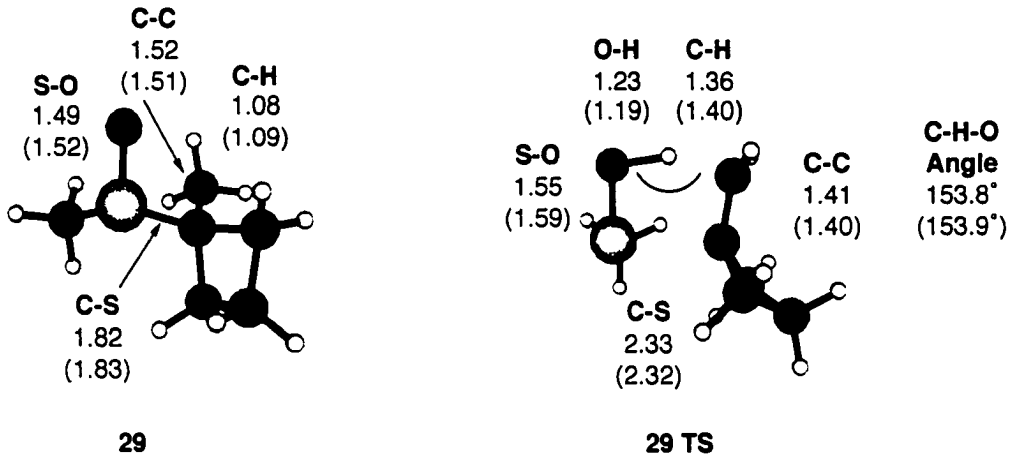



**Figure 23**. Geometry of 1-Methylcyclobutyl Methyl Sulfoxide, **29**, and its transition state, **29 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

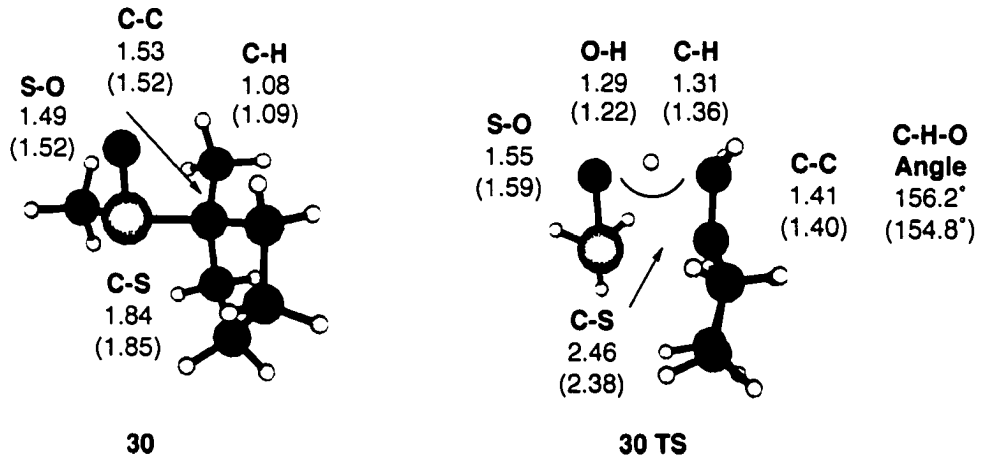



**Figure 24**. Geometry of 1-Methylcyclopentyl Methyl Sulfoxide, **30**, and its transition state, **30 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

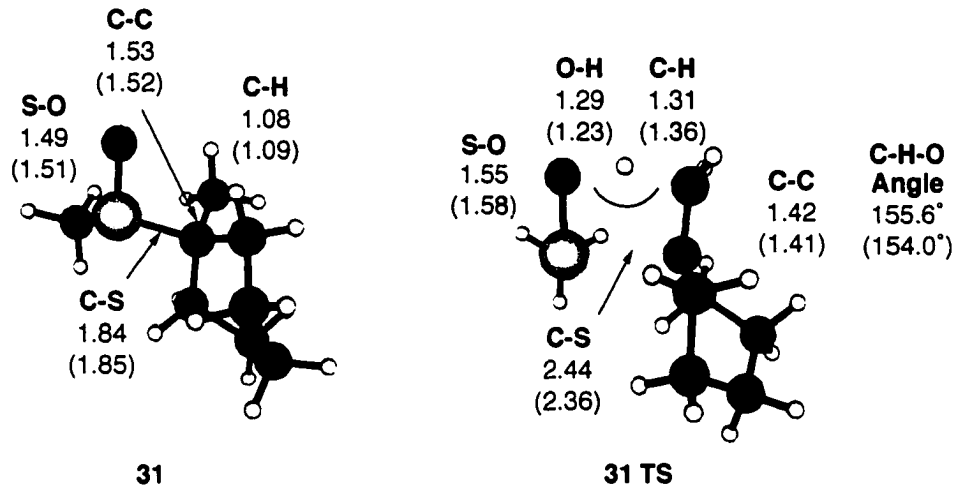



**Figure 25**. Geometry of 1-Methylcyclohexyl Methyl Sulfoxide, **31**, and its transition state, **31 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

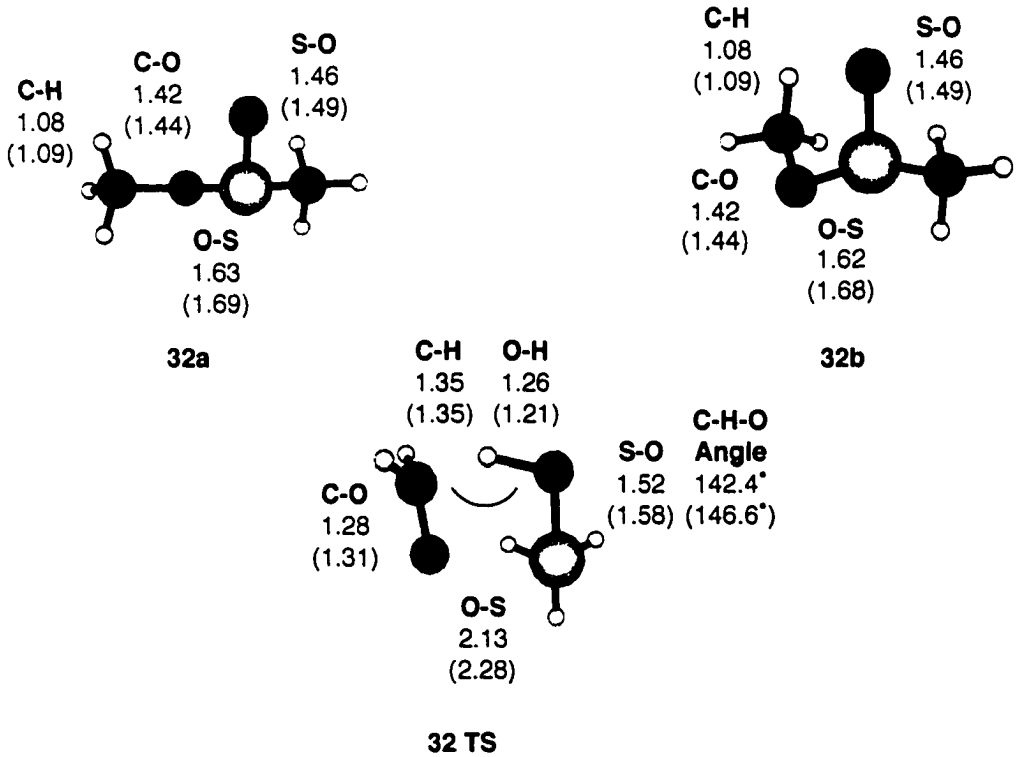



**Figure 26**. Geometry of methyl methanesulfinate, **32a** and **32b** (lowest energy conformer), and its transition state, **32 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

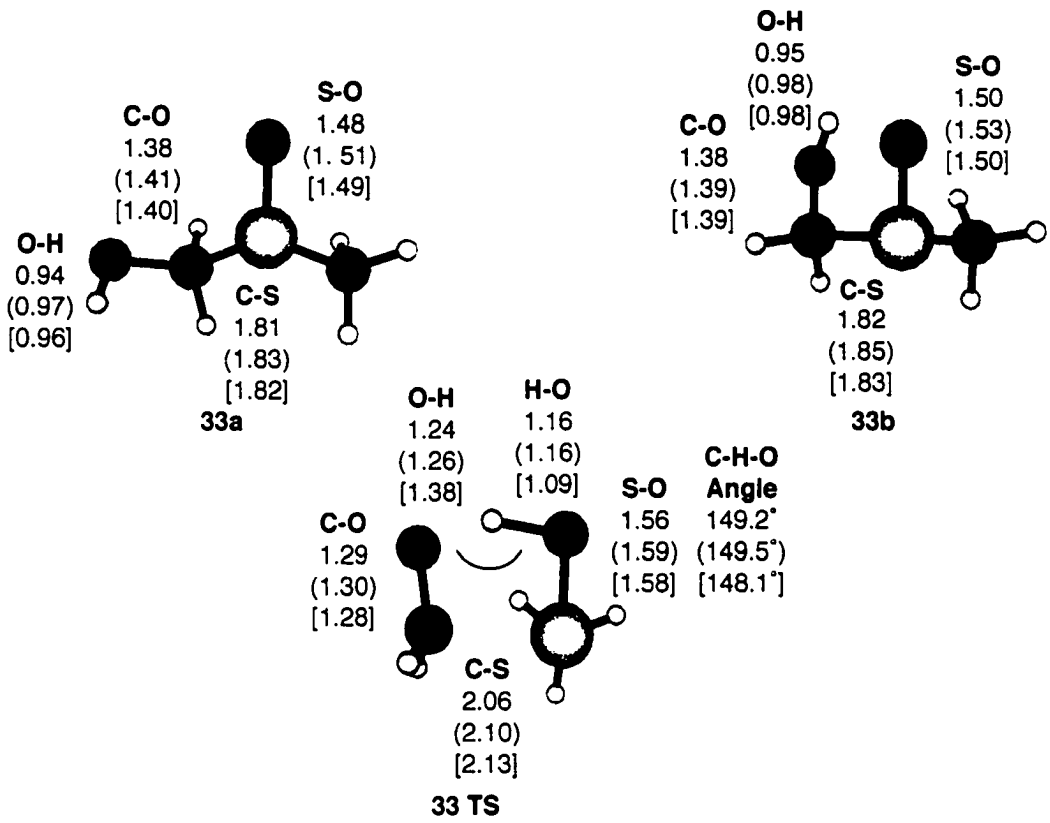



**Figure 27**. Geometry of methylsulfinylmethanol, **33a** and **33b** (lowest energy conformer), and its transition state, **33 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

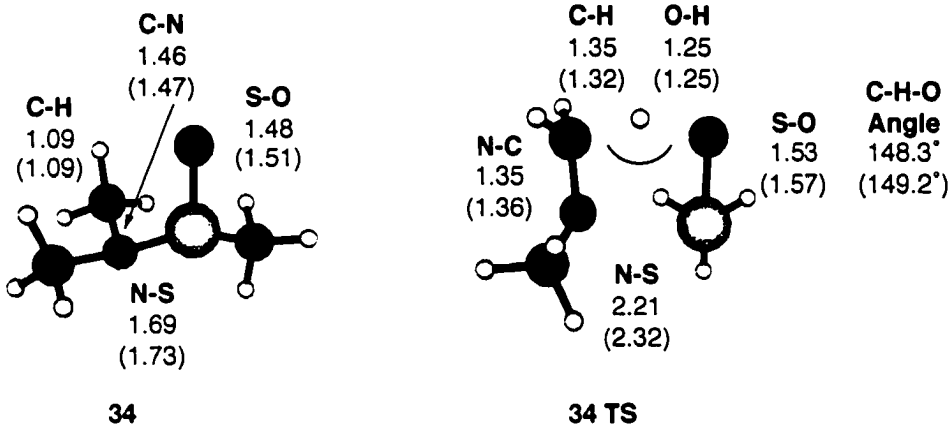



**Figure 28**. Geometry of N,N-dimethyl methanesulfinamide, **34**, and its transition state, **34 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

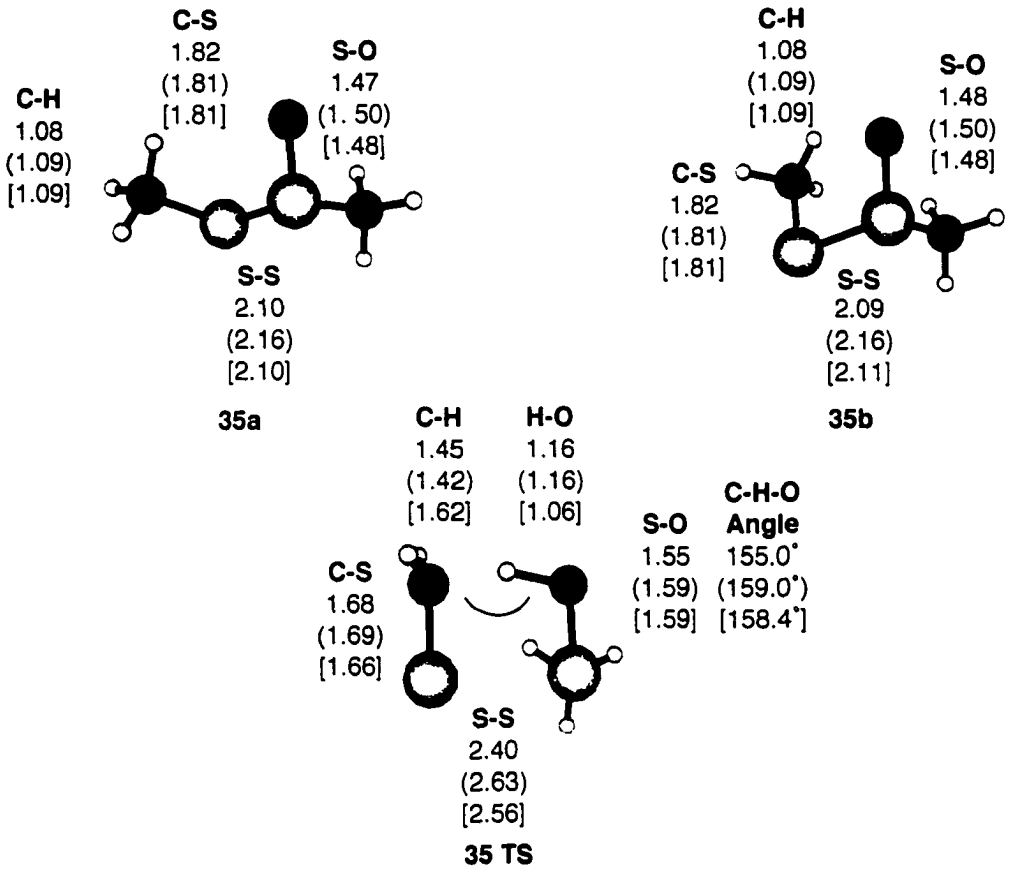


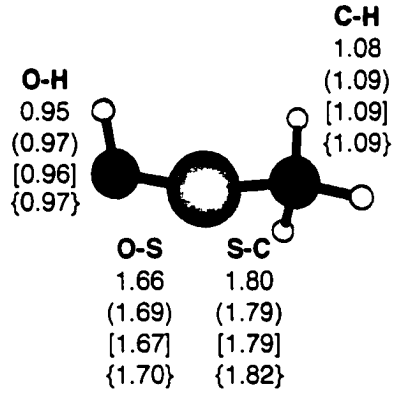

**Figure 29**. Geometry of methylsulfinylmethanol, **35a** (lowest energy conformer) and **35b**, and its transition state, **35 TS**. All bond distances are shown in Å. All bond distances and angles are shown in the following order: HF/6-31G(d,p), and (MP2/6-31G(d,p)), respectively.

# APPENDIX 3

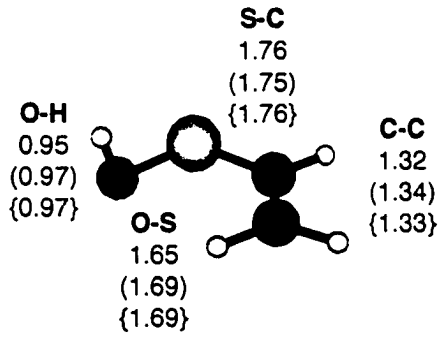
## GEOMETRIES OF SULFENIC ACIDS

Atoms are color coded: Red = oxygen
Gray = carbon
White = hydrogen
Yellow = sulfur
Green = fluorine
Blue = nitrogen

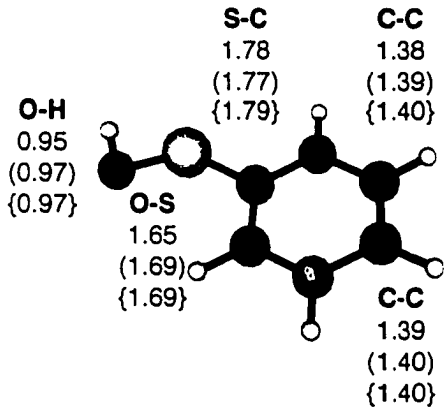
Olefins are labeled as # ene. # refers to which sulfoxide/derivative produce it.



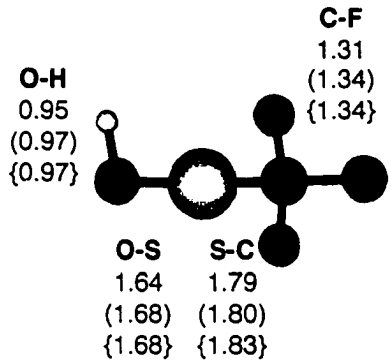

**8, 15, 20 -22, 24 -36 acid**



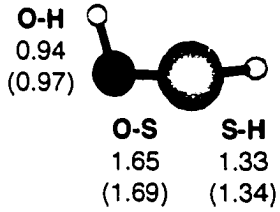

**9, 23 acid**



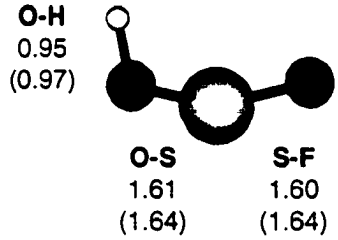

**10 acid**



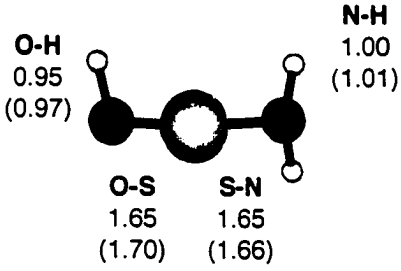

**11 acid**



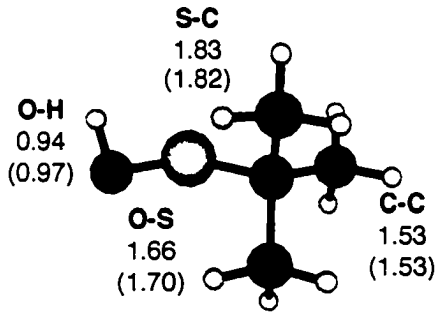

**12 acid**




**13 acid**




**14 acid**



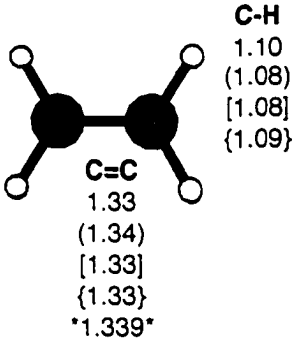

**16 acid**

# APPENDIX 4

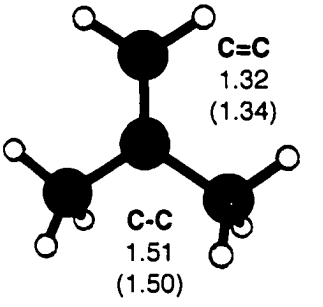
## GEOMETRIES OF OLEFINS

Atoms are color coded: Red = oxygen
Gray = carbon
White = hydrogen
Yellow = sulfur
Green = fluorine
Blue = nitrogen

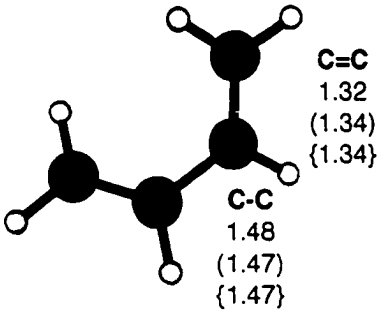
Olefins are labeled as # ene. # refers to which sulfoxide/derivative produced it.



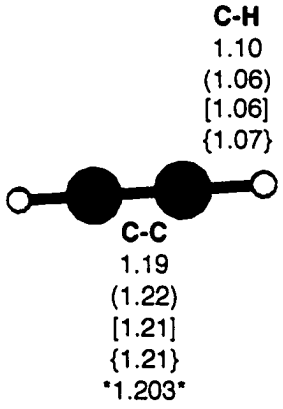

**1 - 14 Ene**



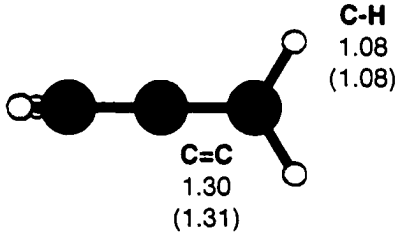

**15** and **16 Ene**



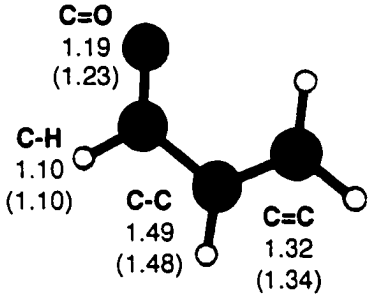

**17 Ene**



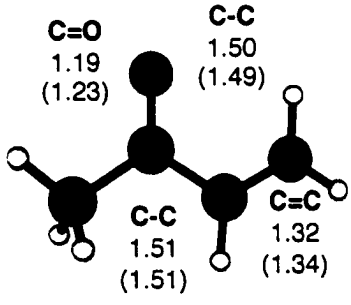

**18 Ene**



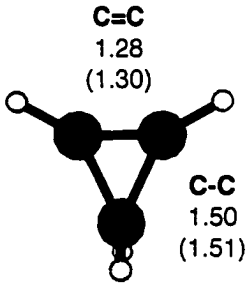

**19 Ene**



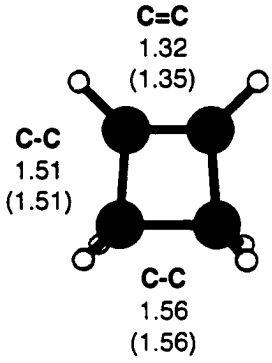

**20** and **21 Ene**



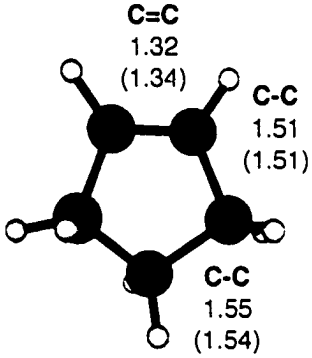

**22** and **23 Ene**



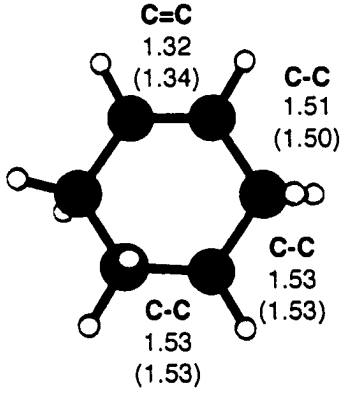

**24 Ene**



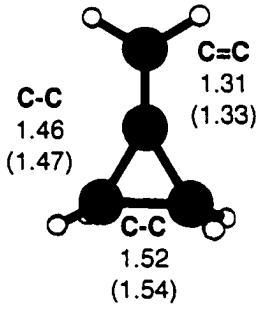

**25 Ene**



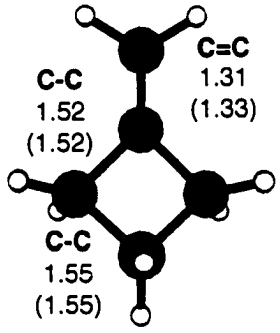

**26 Ene**



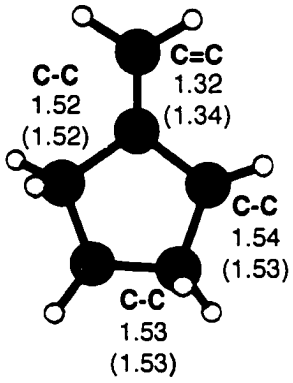

**27 Ene**



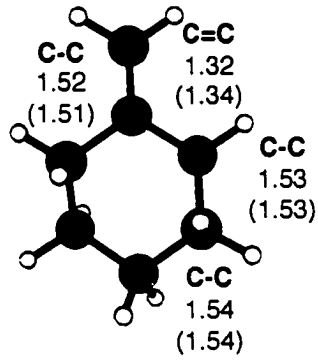

**28 Ene**



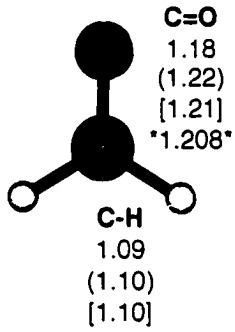

**29 Ene**



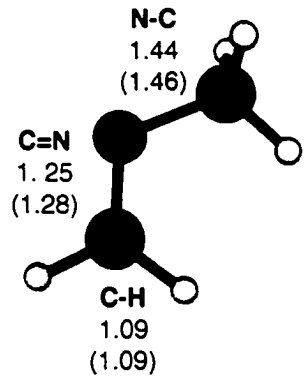

**30 Ene**



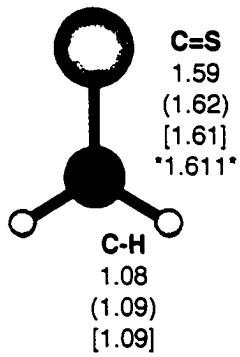

**31 Ene**

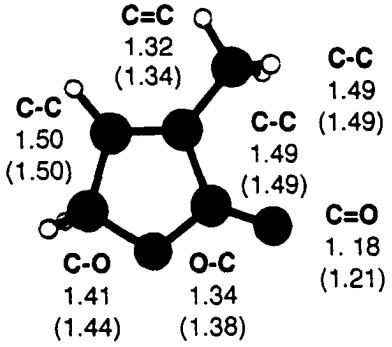



**32** and **33 Ene**

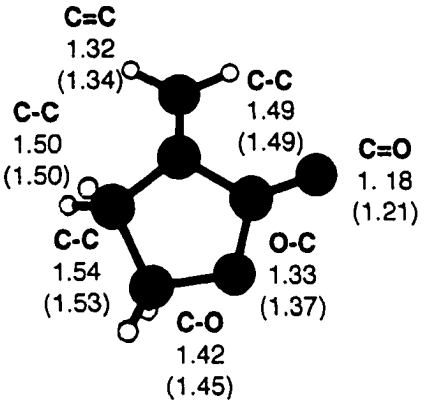



**34 Ene**





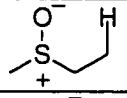
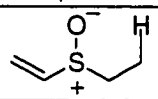
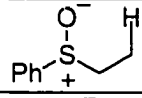
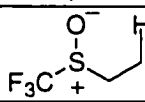
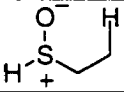
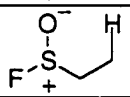
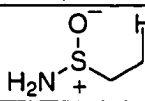
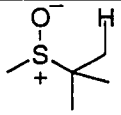
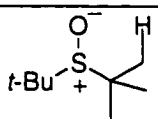
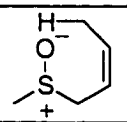
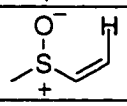
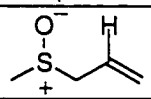
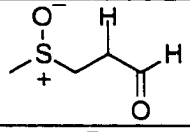
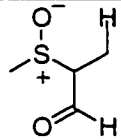

**36 Endo Ene**

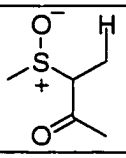
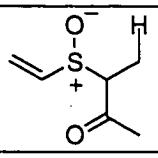
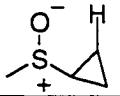
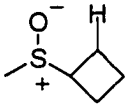
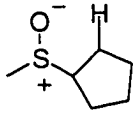
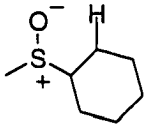
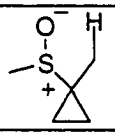
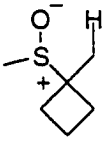
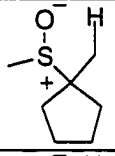
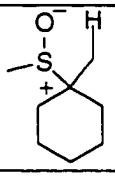
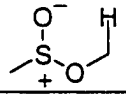
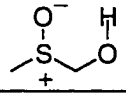
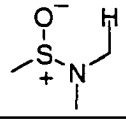


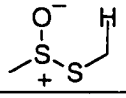

**36 Exo Ene**

# APPENDIX 5

## ACTVIATION ENTHALPIES FOR ALL SULFOXIDES AND DERIVATIVES

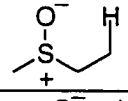
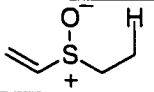
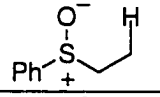
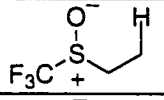
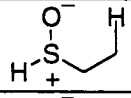
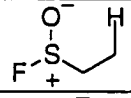
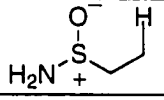
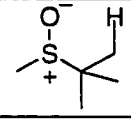
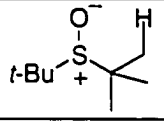
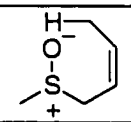
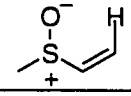
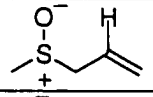
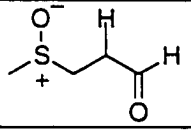
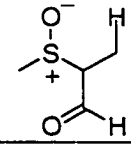
| Sulfoxide | Sulfoxide # | HF/6-31G(d,p) | MP2/6-31G(d,p) | MP2/6-311+G(3df,2p)[a] |
|---|---|---|---|---|
|  | **8** | 44.0 | 28.9 | 32.3 |
|  | **9**-*anti* | 42.0 | 27.3 | ------- |
| | **9**-*syn* | 43.5 | 28.6 | 30.4 |
|  | **10** | 42.7 | 28.5 | 30.6 |
|  | **11** | 41.2 | 27.4 | 30.7 |
|  | **12** | 41.2 | 27.3 | 30.0 |
|  | **13** | 53.0 | 41.5 | 42.7 |
|  | **14** | 47.4 | 32.8 | 35.1 |
|  | **15** | 39.7 | 28.2 | 31.4 |
|  | **16** | 34.5 | 24.1 | 27.4 |
|  | **17** | 54.7 | 53.7 | 47.8 |
|  | **18** | 50.1 | 37.9 | 40.3 |
|  | **19** | 54.7 | 38.0 | 42.8 |
|  | **20** | 32.6 | 18.9 | 22.0 |
|  | **21** | 39.5 | 22.4 | 25.2 |

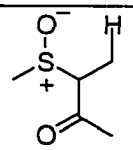
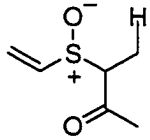
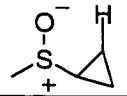
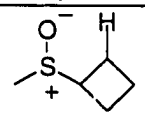
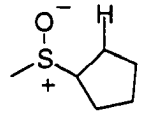
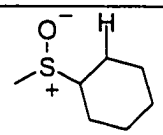
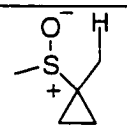
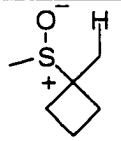
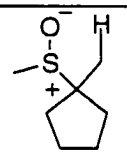
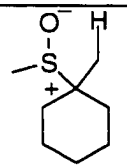
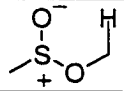
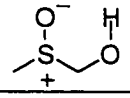
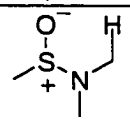
| | | | | |
|---|---|---|---|---|
|  | **22** | 39.2 | 22.9 | 25.3 |
|  | **23** | 40.2 | 22.2 | 23.6 |
|  | **24** | 56.4 | 41.6 | 46.8 |
|  | **25** | 46.0 | 30.7 | 33.8 |
|  | **26** | 40.4 | 24.6 | 28.0 |
|  | **27** | 44.6 | 29.9 | 33.4 |
|  | **28** | 50.1 | 35.9 | 39.6 |
|  | **29** | 42.9 | 29.8 | 33.5 |
|  | **30** | 39.1 | 28.4 | 31.2 |
|  | **31** | 40.0 | 28.6 | 31.8 |
|  | **32a** | 59.9 | 25.5 | 31.5 |
| | **32b** | 60.0 | 26.0 | 32.7 |
|  | **33a** | 9.1 | -1.0 | 5.3 |
| | **33b** | 15.1 | 6.0 | 10.3 |
|  | **34** | 52.0 | 27.3 | 33.2 |

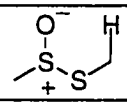
| | | | | |
|---|---|---|---|---|
|  | **35a** | 33.0 | 13.6 | 22.0 |
| | **35b** | 34.0 | 14.7 | 21.3 |

# APPENDIX 6

## HEATS OF REACTION FOR SULFOXIDES AND DERIVATIVES

| Sulfoxide | Sulfoxide # | HF/6-31G(d,p) | MP2/6-31G(d,p) | MP2/6-311+G(3df,2p)[a] |
|---|---|---|---|---|
|  | **8** | 0.4 | 12.8 | 22.6 |
|  | **9**-*anti* | -2.1 | 9.6 | ------- |
| | **9**-*syn* | -0.2 | 12.8 | 20.6 |
|  | **10** | 0.5 | 14.5 | 15.7 |
|  | **11** | -3.5 | 9.8 | 18.0 |
|  | **12** | -5.5 | 7.2 | 20.1 |
|  | **13** | 17.3 | 32.6 | 42.6 |
|  | **14** | 4.2 | 16.5 | 28.9 |
|  | **15** | -5.7 | 12.7 | 22.6 |
|  | **16** | -10.8 | 7.1 | 16.6 |
|  | **17** | -5.2 | 16.6 | 21.1 |
|  | **18** | 15.0 | 20.4 | 28.7 |
|  | **19** | 6.6 | 20.0 | 29.9 |
|  | **20** | -5.7 | 7.7 | 18.8 |
|  | **21** | -5.3 | 10.8 | 21.0 |

| | | | | |
|---|---|---|---|---|
|  | **22** | -6.5 | 10.9 | 21.0 |
|  | **23** | -5.2 | 10.6 | 19.3 |
|  | **24** | 25.3 | 35.6 | 46.1 |
|  | **25** | 2.8 | 16.3 | 25.8 |
|  | **26** | -4.4 | 11.0 | 20.9 |
|  | **27** | -6.3 | 11.1 | 21.2 |
|  | **28** | 9.0 | 25.5 | 35.5 |
|  | **29** | -2.4 | 16.7 | 27.1 |
|  | **30** | -6.5 | 13.1 | 23.4 |
|  | **31** | -6.2 | 14.2 | 24.6 |
|  | **32a** | -13.6 | 0.2 | 11.3 |
| | **32b** | -13.5 | 0.7 | 12.6 |
|  | **33a** | -16.3 | -6.0 | 8.2 |
| | **33b** | -10.3 | 1.1 | 12.4 |
|  | **34** | -10.4 | 4.6 | 17.0 |

| | | | | |
|---|---|---|---|---|
|  | **35a** | -1.8 | 10.3 | 27.4 |
| | **35b** | -0.8 | 11.4 | 26.8 |

# APPENDIX 7

## INTRINSIC REACTION COORDINATES

Atoms are color coded: Red = oxygen
Gray = carbon
White = hydrogen
Yellow = sulfur
Blue = nitrogen

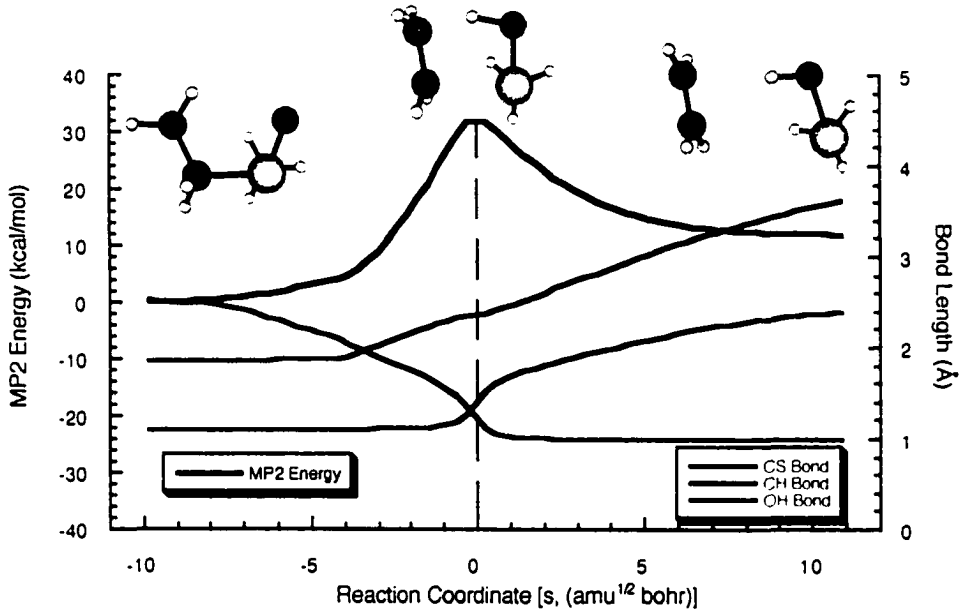



**Figure 1**. IRC of ethyl methyl sufoxide (**8**) at MP2/6-31G(d,p)

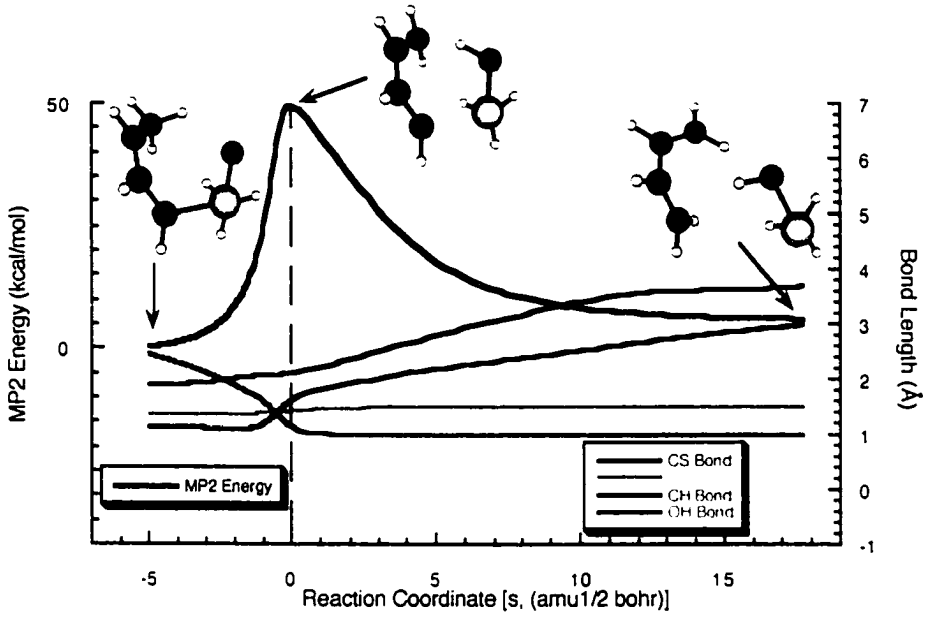



**Figure 2.** IRC of (Z)-2-butenyl methyl sufoxide (**17**) at MP2/6-31G(d,p)

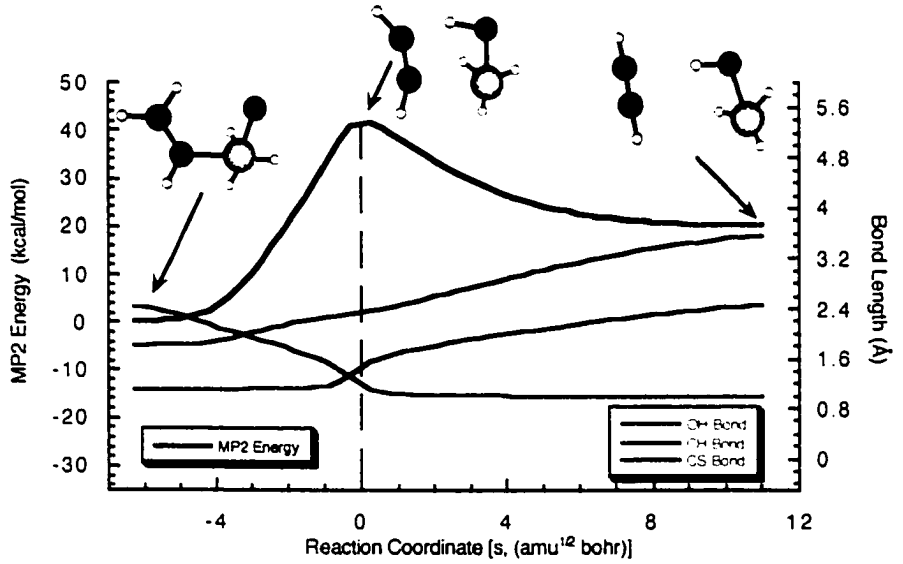



**Figure 3.** IRC of methyl vinyl sufoxide (**18**) at MP2/6-31G(d,p)

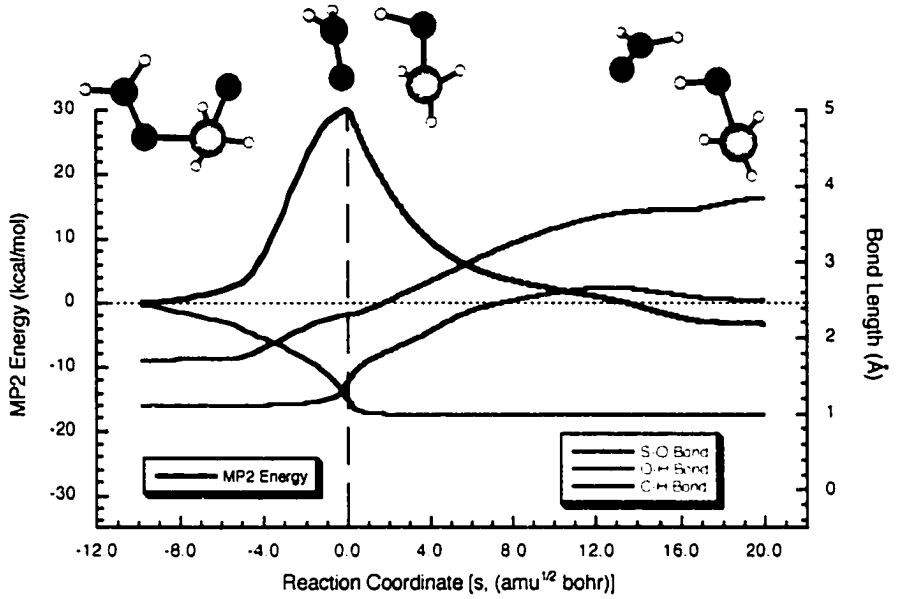



**Figure 4**. IRC of methyl methanesulfinate (**32**) at MP2/6-31G(d,p)

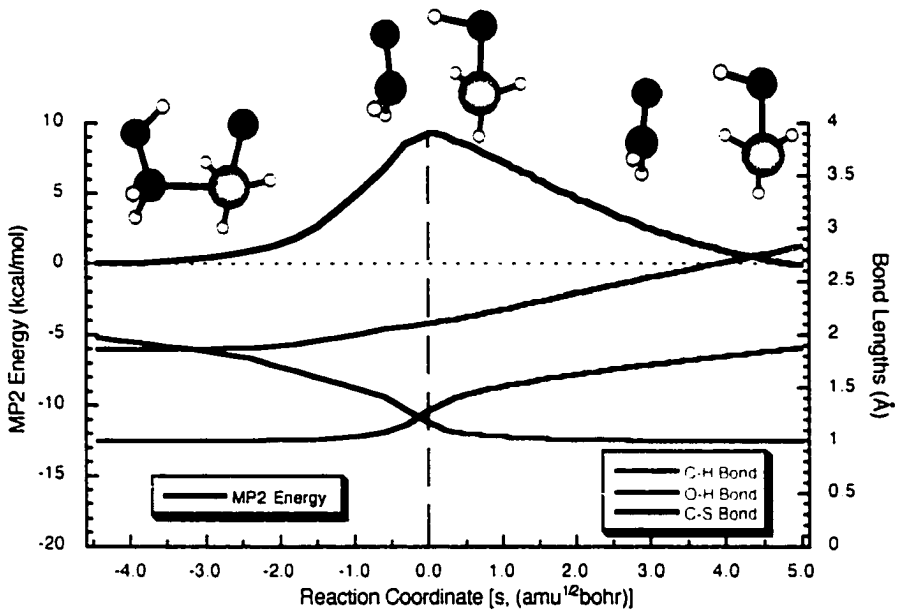



**Figure 5**. IRC of methanesulfinylmethanol (**33**) at MP2/6-31G(d,p)

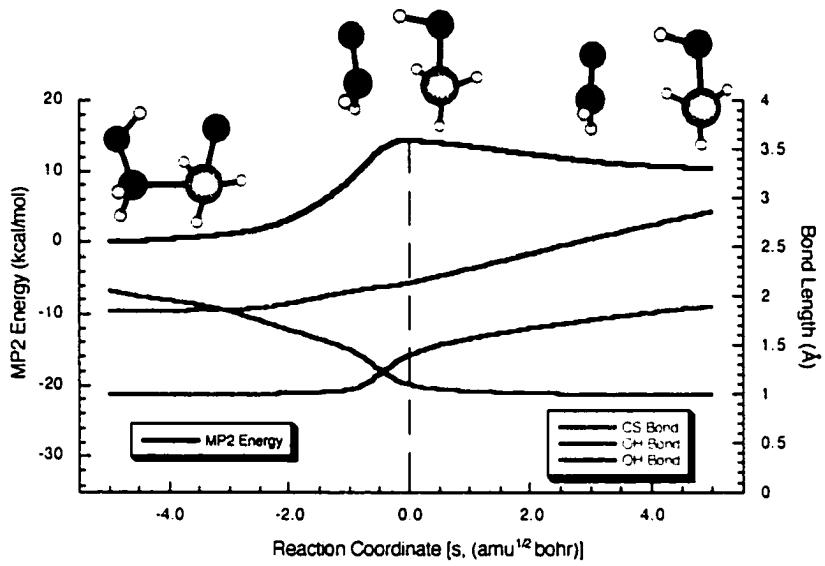



**Figure 6**. IRC of methanesulfinylmethanol (**33**) at MP2/6-311+G(3df,2p)

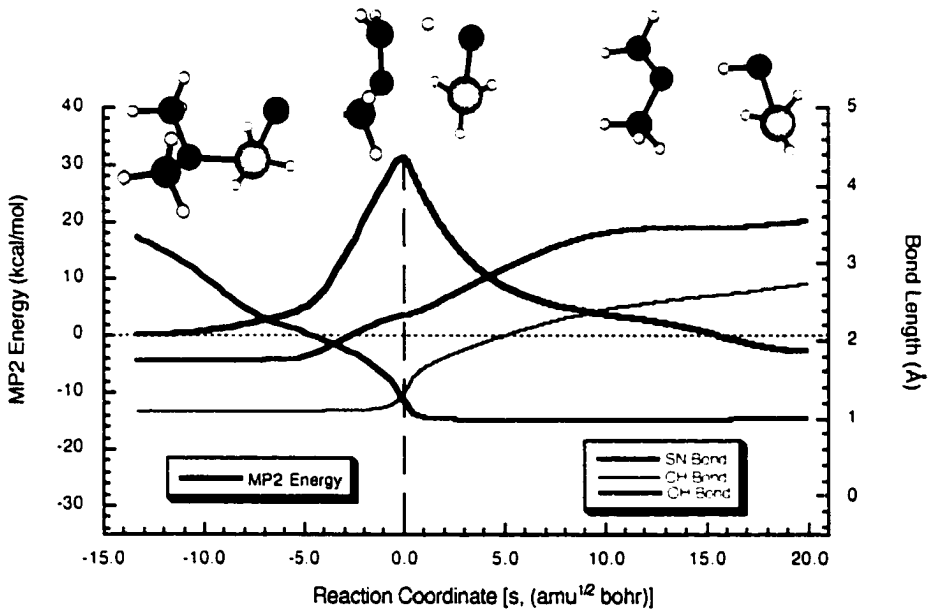



**Figure 7**. IRC of N,N-dimethyl methanesulfinamide (**34**) at MP2/6-31G(d,p)

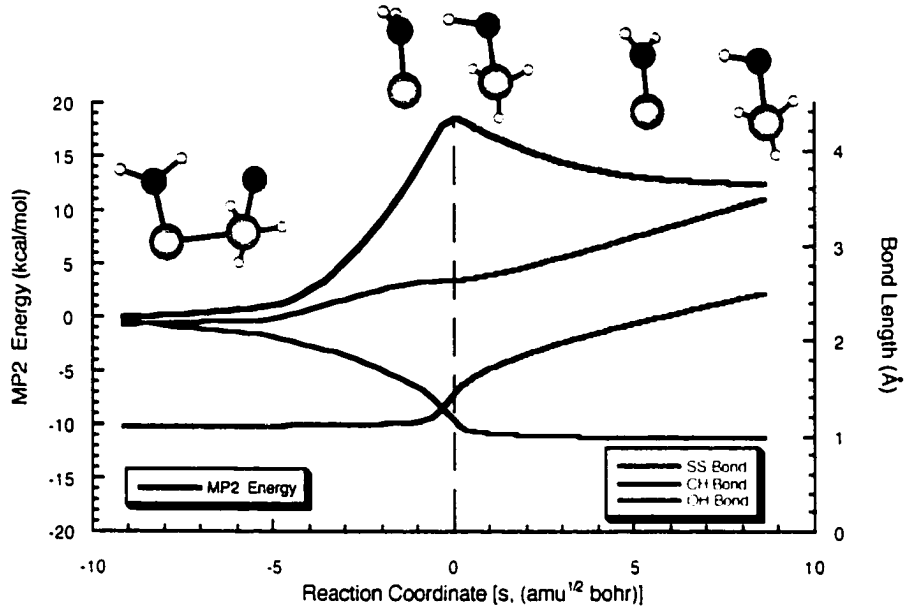



**Figure 8**. IRC of methyl thiomethanesulfinate (**35**) at MP2/6-31G(d,p)

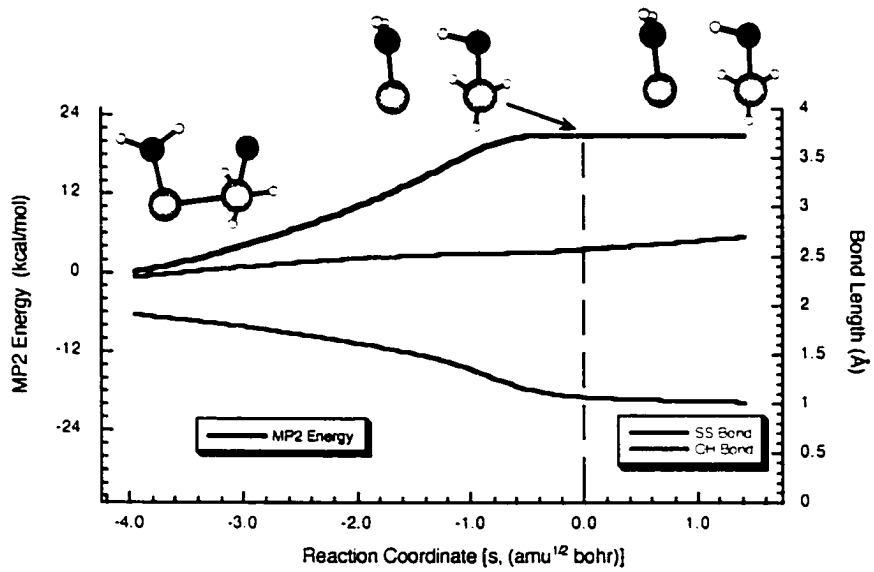



**Figure 9**. IRC of methyl thiomethanesulfinate (**35**) at MP2/6-311+G(3df,2p)

# APPENDIX 8

## COORDINATES FOR SULFOXIDES AND DERIVATIVES IN CHAPTER 1

**Ethyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.7980157591 | 1.6413874597 | -2.0662442709 |
| C | 6.0 | 0.7115794566 | 1.5651175381 | -0.9904315232 |
| H | 1.0 | 1.7006470192 | 1.4746831027 | -0.5586829748 |
| S | 16.0 | -0.2402618190 | 0.0859219142 | -0.6330888810 |
| H | 1.0 | 0.2013435612 | 2.4396648888 | -0.6045582780 |
| O | 8.0 | 0.5964416829 | -1.0716639697 | -1.0492623366 |
| C | 6.0 | -0.1546711828 | 0.1621231691 | 1.1676586151 |
| H | 1.0 | 0.8935369724 | 0.2175670199 | 1.4415085280 |
| C | 6.0 | -0.8094386099 | -1.0685591159 | 1.7867758552 |
| H | 1.0 | -0.6493859657 | 1.0762505282 | 1.4812348216 |
| H | 1.0 | -0.3299067709 | -1.9702777296 | 1.4273532202 |
| H | 1.0 | -1.8656646378 | -1.1189075779 | 1.5425596259 |
| H | 1.0 | -0.7135154654 | -1.0334412276 | 2.8663875985 |

| | |
|---|---|
| Energy | -590.5864345 Hartree |
| ZPE | 0.115810 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.8028485119 | 1.6624309878 | -2.0524643680 |
| C | 6.0 | 0.7284698640 | 1.5479674392 | -0.9740532001 |
| H | 1.0 | 1.7217747580 | 1.3939748838 | -0.5558410761 |
| S | 16.0 | -0.2820400559 | 0.0849351131 | -0.6467010147 |
| H | 1.0 | 0.2578662374 | 2.4292249227 | -0.5408536720 |
| O | 8.0 | 0.5264926627 | -1.1291225265 | -1.0514991139 |
| C | 6.0 | -0.1892857607 | 0.1977247244 | 1.1645523048 |
| H | 1.0 | 0.8633689590 | 0.3013281089 | 1.4339657924 |
| C | 6.0 | -0.7826155285 | -1.0602822030 | 1.7770075965 |
| H | 1.0 | -0.7260402809 | 1.0982614343 | 1.4690830768 |
| H | 1.0 | -0.2533173401 | -1.9335870746 | 1.4025542645 |
| H | 1.0 | -1.8374320504 | -1.1614573903 | 1.5245641012 |
| H | 1.0 | -0.6913699766 | -1.0315324196 | 2.8608953086 |

| | |
|---|---|
| Energy | -591.3448371 Hartree |
| ZPE | 0.111840 Hartree/Molecule |
| CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p) | -591.4220497 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -591.6630465 Hartree |

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1 | -2.737125 | -0.345178 | -0.109486 |
| C | 6 | -1.801788 | -0.844253 | 0.147324 |
| H | 1 | -1.727694 | -0.965583 | 1.230274 |
| S | 16 | -0.458770 | 0.239233 | -0.427084 |
| H | 1 | -1.742429 | -1.807751 | -0.364835 |
| O | 8 | -0.514098 | 1.476589 | 0.408176 |
| C | 6 | 0.923262 | -0.775788 | 0.218355 |
| H | 1 | 0.731808 | -0.921283 | 1.286054 |
| C | 6 | 2.256830 | -0.073579 | -0.022690 |
| H | 1 | 0.869688 | -1.742603 | -0.293293 |
| H | 1 | 2.263939 | 0.909266 | 0.453488 |
| H | 1 | 2.450600 | 0.058966 | -1.090823 |
| H | 1 | 3.074503 | -0.664558 | 0.398614 |

Energy -592.5139058 Hartree
ZPE 0.108285 Hartree/Molecule

**Transition State for Ethyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.0386913609 | -0.6547436716 | -1.7938841909 |
| S | 16.0 | -0.8486513267 | 0.0861102703 | -0.3712852011 |
| O | 8.0 | -0.6808984818 | -0.9812127556 | 0.7405221872 |
| C | 6.0 | 0.9339237979 | 1.2431541996 | 0.4684613424 |
| H | 1.0 | -0.6072901995 | -1.5130590555 | -2.1255174470 |
| H | 1.0 | 0.9637691179 | -0.9682381631 | -1.5314469674 |
| H | 1.0 | -0.0007838507 | 0.0822244204 | -2.5885908362 |
| C | 6.0 | 1.3423013907 | 0.3482566129 | 1.4783038786 |
| H | 1.0 | 0.4012514617 | 2.1399615818 | 0.7290476134 |
| H | 1.0 | 1.4847638065 | 1.3201003948 | -0.4529547880 |
| H | 1.0 | 1.2047513035 | 0.6758360741 | 2.4973486044 |
| H | 1.0 | 2.2563702329 | -0.1985635841 | 1.3037327398 |
| H | 1.0 | 0.3264498085 | -0.5707486240 | 1.2986918647 |

Energy -590.5100643 Hartree
ZPE 0.109673 Hartree/Molecule
Imaginary Frequency -1787.67 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.0289022196 | -0.6391540949 | -1.7673487025 |
| S | 16.0 | -0.9126295792 | 0.0752567056 | -0.3698073900 |
| O | 8.0 | -0.6907952067 | -0.9929692680 | 0.7785983437 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.9446654200 | 1.2516498479 | 0.4475172539 |
| H | 1.0 | -0.5365300915 | -1.5383348774 | -2.1058437729 |
| H | 1.0 | 0.9891689913 | -0.8840899493 | -1.4717317495 |
| H | 1.0 | -0.0114721758 | 0.0964387880 | -2.5714365628 |
| C | 6.0 | 1.3386198523 | 0.3480938229 | 1.4453869018 |
| H | 1.0 | 0.4282452984 | 2.1636744233 | 0.7178480418 |
| H | 1.0 | 1.4836221201 | 1.3048313271 | -0.4909552760 |
| H | 1.0 | 1.1973908091 | 0.6453347711 | 2.4772124223 |
| H | 1.0 | 2.2186575190 | -0.2562866934 | 1.2619436117 |
| H | 1.0 | 0.3172249623 | -0.5653671030 | 1.3010456783 |

| | |
|---|---|
| Energy | -591.2923609 Hartree |
| ZPE | 0.105618 Hartree/Molecule |
| Imaginary Frequency | -1103.52 $cm^{-1}$ |
| CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) | -591.3685431 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -591.6052089 Hartree |

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6 | -1.674800 | -0.789226 | 0.603651 |
| S | 16 | -0.757569 | 0.237339 | -0.577509 |
| O | 8 | -0.131655 | 1.371451 | 0.300890 |
| C | 6 | 1.372919 | -0.914877 | -0.411835 |
| H | 1 | -2.503104 | -0.212753 | 1.018423 |
| H | 1 | -1.016385 | -1.129219 | 1.405273 |
| H | 1 | -2.065256 | -1.649173 | 0.051370 |
| C | 6 | 2.013906 | -0.005565 | 0.444887 |
| H | 1 | 1.574929 | -0.910307 | -1.476388 |
| H | 1 | 0.955881 | -1.843103 | -0.036863 |
| H | 1 | 2.805756 | 0.613369 | 0.029003 |
| H | 1 | 2.158673 | -0.293031 | 1.483809 |
| H | 1 | 0.991706 | 0.913192 | 0.538176 |

| | |
|---|---|
| Energy | -592.470419 Hartree |
| ZPE | 0.102461 Hartree/Molecule |
| Imaginary Frequency | -1145.44 $cm^{-1}$ |

**Methanesulfenic Acid**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -0.1340971401 | 0.3217035174 | -0.4314332458 |
| C | 6.0 | -0.3134550018 | 0.4443058425 | 1.3517900641 |
| H | 1.0 | 0.6483654436 | 0.4956087057 | 1.8460950133 |
| H | 1.0 | -0.8813150846 | -0.3937844556 | 1.7328120973 |
| H | 1.0 | -0.8585179248 | 1.3615307711 | 1.5465670166 |

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 0.6078598440 | -1.1532268264 | -0.5523004620 |
| H | 1.0 | 1.5445902158 | -1.0278538888 | -0.5602785023 |

| | |
|---|---|
| Energy | -512.5418924 Hartree |
| ZPE | 0.056228 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -0.1387071135 | 0.3384267167 | -0.4351587798 |
| C | 6.0 | -0.3113611882 | 0.4461945311 | 1.3480378877 |
| H | 1.0 | 0.6535561444 | 0.4978448065 | 1.8471492342 |
| H | 1.0 | -0.8805197499 | -0.3986070701 | 1.7267426541 |
| H | 1.0 | -0.8615887424 | 1.3643403099 | 1.5542010938 |
| O | 8.0 | 0.5990092425 | -1.1820073904 | -0.5547800341 |
| H | 1.0 | 1.5530417592 | -1.0179082378 | -0.5529400746 |

| | |
|---|---|
| Energy | -513.0011202 Hartree |
| ZPE | 0.053749 Hartree/Molecule |
| CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) | -513.0476908 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -513.2241254 Hartree |

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16 | -0.087970 | -0.604170 | 0.005051 |
| C | 6 | 1.384081 | 0.439966 | -0.000106 |
| H | 1 | 1.441915 | 1.065556 | 0.893325 |
| H | 1 | 1.419118 | 1.054173 | -0.901922 |
| H | 1 | 2.232071 | -0.252595 | -0.005031 |
| O | 8 | -1.301076 | 0.548406 | -0.106914 |
| H | 1 | -1.581458 | 0.772544 | 0.788757 |

| | |
|---|---|
| Energy | -513.9008139 Hartree |
| ZPE | 0.052264 Hartree/Molecule |

**Ethylene**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -.0000000042 | .9153882646 | 1.2245537659 |
| C | 6.0 | .0000000007 | -.0000003683 | .6582259521 |
| C | 6.0 | -.0000000081 | .0000003661 | -.6582259527 |
| H | 1.0 | .0000000056 | -.9153880462 | 1.2245537385 |
| H | 1.0 | .0000000080 | .9153880469 | -1.2245537389 |
| H | 1.0 | -.0000000019 | -.9153882631 | -1.2245537649 |

| | |
|---|---|
| Energy | -78.0388415 Hartree |
| ZPE | 0.054491 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.0000000623 | 0.9240144599 | 1.2314596683 |
| C | 6.0 | 0.0000003097 | -0.0000027722 | 0.6668752100 |
| C | 6.0 | -0.0000005140 | 0.0000024002 | -0.6668752423 |
| H | 1.0 | -0.0000000573 | -0.9240128241 | 1.2314595013 |
| H | 1.0 | 0.0000001645 | 0.9240129893 | -1.2314595841 |
| H | 1.0 | 0.0000001594 | -0.9240142532 | -1.2314595532 |

| | |
|---|---|
| Energy | -78.3172748 Hartree |
| ZPE | 0.052270 Hartree/Molecule |
| CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) | -78.3557116 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -78.3900295 Hartree |

Becke3/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1 | 0.000000 | 0.922361 | 1.237374 |
| C | 6 | 0.000000 | 0.000000 | 0.665406 |
| C | 6 | 0.000000 | 0.000000 | -0.665406 |
| H | 1 | 0.000000 | -0.922361 | 1.237374 |
| H | 1 | 0.000000 | 0.922361 | -1.237374 |
| H | 1 | 0.000000 | -0.922361 | -1.237374 |

| | |
|---|---|
| Energy | -78.5937978 Hartree |
| ZPE | 0.050995 Hartree/Molecule |

**Ethyl Vinyl Sulfoxide**

Lowest Energy Conformer-Vinyl substituent *syn* with sulfinyl substituent

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.5399799417 | -0.1717576684 | -1.3281380164 |
| S | 16.0 | -0.4280954339 | -0.7435250615 | 0.0488540861 |
| O | 8.0 | 0.5225110607 | -1.0831155244 | 1.1412267039 |
| C | 6.0 | -1.2202392265 | 0.8212258866 | 0.5041048411 |
| C | 6.0 | -0.2578726239 | 1.8627840240 | 1.0594875375 |
| H | 1.0 | -1.9564427839 | 0.5444685377 | 1.2507810036 |
| H | 1.0 | -1.7575444259 | 1.1723671455 | -0.3715689326 |
| H | 1.0 | 0.4309612774 | 2.2134462193 | 0.3005946005 |
| H | 1.0 | 0.3156375821 | 1.4415891989 | 1.8746618107 |
| H | 1.0 | -0.8174355144 | 2.7149335750 | 1.4312726516 |
| C | 6.0 | 1.8521348633 | -0.2566374770 | -1.3110437028 |
| H | 1.0 | -0.0256820832 | 0.1713004185 | -2.1780963376 |
| H | 1.0 | 2.4385710728 | 0.0369347063 | -2.1632813659 |
| H | 1.0 | 2.3615625978 | -0.6268086174 | -0.4399603466 |

| | |
|---|---|
| Energy | -628.4289389 Hartree |
| ZPE | 0.121897 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .5004519385 | -.1563152807 | -1.3210429150 |
| S | 16.0 | -.4391007626 | -.7732511743 | .0710095852 |
| O | 8.0 | .5514194863 | -1.0835055665 | 1.1747870789 |
| C | 6.0 | -1.2284671493 | .8200778334 | .4890480954 |
| C | 6.0 | -.2301889591 | 1.8290729436 | 1.0256407636 |
| H | 1.0 | -1.9757907516 | .5710838057 | 1.2432893273 |
| H | 1.0 | -1.7523640858 | 1.1653463149 | -.4043286999 |
| H | 1.0 | .4583599273 | 2.1543652092 | .2491756535 |
| H | 1.0 | .3485150780 | 1.3739362159 | 1.8267564129 |
| H | 1.0 | -.7510234540 | 2.7006458877 | 1.4179275431 |
| C | 6.0 | 1.8331924306 | -.2090303176 | -1.2775090591 |
| H | 1.0 | -.0749062694 | .1740753281 | -2.1778945426 |
| H | 1.0 | 2.4383722088 | .1082429405 | -2.1141464281 |
| H | 1.0 | 2.3195766665 | -.5775387767 | -.3838182822 |

| | |
|---|---|
| Energy | -629.3089007 Hartree |
| ZPE | 0.116974 Hartree/Molecule |
| CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) | -629.3978538 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -629.6615516 Hartree |

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6 | 0.464020 | -0.167919 | -1.403028 |
| S | 16 | -0.500418 | -0.778393 | 0.001063 |
| O | 8 | 0.478392 | -1.109936 | 1.109347 |
| C | 6 | -1.309244 | 0.839337 | 0.436599 |
| C | 6 | -0.322372 | 1.855853 | 0.993461 |
| H | 1 | -2.063254 | 0.564929 | 1.181060 |
| H | 1 | -1.832192 | 1.182447 | -0.462983 |
| H | 1 | 0.360711 | 2.214068 | 0.219231 |
| H | 1 | 0.271681 | 1.396427 | 1.788078 |
| H | 1 | -0.857737 | 2.715013 | 1.409052 |
| C | 6 | 1.789927 | -0.249731 | -1.372141 |
| H | 1 | -0.117979 | 0.170695 | -2.257452 |
| H | 1 | 2.399965 | 0.050061 | -2.218416 |
| H | 1 | 2.284383 | -0.625106 | -0.479701 |

| | |
|---|---|
| Energy | -630.5919745 Hartree |
| ZPE | 0.113678 Hartree/Molecule |

Higher Energy Conformer-Vinyl substituent *anti* with sulfinyl substituent

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.6223571125 | -0.0892779944 | -1.2790781491 |
| S | 16.0 | -0.4476546340 | -0.6689014944 | 0.0159491427 |
| O | 8.0 | 0.4209539605 | -1.3215142408 | 1.0318290834 |
| C | 6.0 | -0.9458819896 | 0.9230672283 | 0.7224294967 |
| C | 6.0 | 0.1901657196 | 1.7016549709 | 1.3751727866 |
| H | 1.0 | -1.6958512132 | 0.6624037246 | 1.4617337058 |
| H | 1.0 | -1.4362448226 | 1.4819024693 | -0.0676626311 |
| H | 1.0 | 0.8850205527 | 2.0912330674 | 0.6397434329 |
| H | 1.0 | 0.7322116005 | 1.0642698866 | 2.0614342306 |
| H | 1.0 | -0.2139906838 | 2.5433821829 | 1.9275810841 |
| C | 6.0 | 0.2638152372 | -0.1555308276 | -2.5440309470 |
| H | 1.0 | 1.5885744207 | 0.2609043901 | -0.9593063813 |
| H | 1.0 | 0.9202699199 | 0.1801650964 | -3.3271004556 |
| H | 1.0 | -0.6924994803 | -0.5485044593 | -2.8435641990 |

Energy -628.4254109 Hartree
ZPE 0.116974 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.61773 | -0.05956 | -1.25061 |
| S | 16.0 | -0.44577 | -0.69176 | 0.03902 |
| O | 8.0 | 0.44085 | -1.32889 | 1.08843 |
| C | 6.0 | -0.95473 | 0.93029 | 0.70429 |
| C | 6.0 | 0.19443 | 1.68183 | 1.35274 |
| H | 1.0 | -1.72157 | 0.69232 | 1.44314 |
| H | 1.0 | -1.42491 | 1.47927 | -0.11298 |
| H | 1.0 | 0.89135 | 2.06499 | 0.61015 |
| H | 1.0 | 0.73112 | 1.01209 | 2.02212 |
| H | 1.0 | -0.18347 | 2.52439 | 1.92894 |
| C | 6.0 | 0.25714 | -0.14344 | -2.53507 |
| H | 1.0 | 1.58002 | 0.31752 | -0.92492 |
| H | 1.0 | 0.90199 | 0.21795 | -3.32368 |
| H | 1.0 | -0.69293 | -0.57173 | -2.82645 |

Energy -629.3089007 Hartree
ZPE 0.116794 Hartree/Molecule
CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) -629.3931300 Hartree

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6 | 0.664789 | -0.069228 | -1.254599 |
| S | 16 | -0.396770 | -0.692185 | 0.071414 |
| 0 | 8 | 0.501927 | -1.342707 | 1.103887 |

| | | | | |
|---|---|---|---|---|
| C | 6 | -0.902474 | 0.955449 | 0.769003 |
| C | 6 | 0.237890 | 1.683080 | 1.470269 |
| H | 1 | -1.697556 | 0.701791 | 1.478014 |
| H | 1 | -1.346592 | 1.522774 | -0.055025 |
| H | 1 | 0.959194 | 2.091794 | 0.757204 |
| H | 1 | 0.762470 | 0.992394 | 2.136448 |
| H | 1 | -0.152776 | 2.513150 | 2.066385 |
| C | 6 | 0.311162 | -0.206069 | -2.530163 |
| H | 1 | 1.619547 | 0.341001 | -0.932230 |
| H | 1 | 0.954325 | 0.136049 | -3.335979 |
| H | 1 | -0.633913 | -0.661732 | -2.815601 |

Energy -630.587966 Hartree
ZPE 0.113344 Hartree/Molecule

**Transition State for Ethyl Vinyl Sulfoxide**

Lowest Energy Conformer-Vinyl substituent *syn* with sulfinyl substituent

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.0436977730 | 0.2637376395 | -1.5211298235 |
| S | 16.0 | -0.8884629543 | -0.6726576132 | -0.3494172302 |
| O | 8.0 | 0.0735864899 | -0.879320 2888 | 0.8433028559 |
| C | 6.0 | -1.8619501761 | 1.1211763064 | 0.7738739467 |
| C | 6.0 | -1.0068788484 | 1.1621016810 | 1.8911724229 |
| H | 1.0 | -2.8453397328 | 0.6954684006 | 0.8588471864 |
| H | 1.0 | -1.7504780262 | 1.8281660018 | -0.0279469622 |
| H | 1.0 | -0.2538377445 | 0.0851731485 | 1.5704772784 |
| H | 1.0 | -1.4411831858 | 0.8866097650 | 2.8403079782 |
| H | 1.0 | -0.3107493743 | 1.9853789519 | 1.9378090184 |
| C | 6.0 | 1.3018918227 | 0.6143775056 | -1.3575377393 |
| H | 1.0 | -0.5181906847 | 0.5133609355 | -2.4064423922 |
| H | 1.0 | 1.8153615503 | 1.1799295032 | -2.1141564340 |
| H | 1.0 | 1.8463072912 | 0.3358399631 | -0.4746002057 |

Energy -628.3537209 Hartree
ZPE 0.115510 Hartree/Molecule
Imaginary Frequency -1796.92 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.0007278746 | 0.2489943018 | -1.5020465056 |
| S | 16.0 | -0.9172685570 | -0.7456301660 | -0.3657020744 |
| O | 8.0 | 0.0700111230 | -0.9274892618 | 0.8531836614 |
| C | 6.0 | -1.8472461011 | 1.1243411761 | 0.7348491516 |
| C | 6.0 | -0.9593480644 | 1.1651872228 | 1.8209245063 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.8469010269 | 0.7296648748 | 0.8658444286 |
| H | 1.0 | -1.7325931323 | 1.8134120328 | -0.0920397866 |
| H | 1.0 | -0.2329806245 | 0.0605974662 | 1.5413656121 |
| H | 1.0 | -1.3518837268 | 0.9059865493 | 2.7968962616 |
| H | 1.0 | -0.2096033870 | 1.9467563463 | 1.8243052293 |
| C | 6.0 | 1.2494295220 | 0.6593342444 | -1.2661626057 |
| H | 1.0 | -0.5474808199 | 0.4958785190 | -2.4052120288 |
| H | 1.0 | 1.7729068675 | 1.2735630535 | -1.9835796302 |
| H | 1.0 | 1.7574600018 | 0.3687455409 | -0.3580663198 |

| | |
|---|---|
| Energy | -629.2569451 Hartree |
| ZPE | 0.110513 Hartree/Molecule |
| Imaginary Frequency | -1129.46 $cm^{-1}$ |
| CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) | -629.3447728 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -629.6065023 Hartree |

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6 | 0.511813 | 0.093318 | -1.588010 |
| S | 16 | -0.413482 | -0.871630 | -0.405200 |
| O | 8 | 0.554415 | -1.042356 | 0.829123 |
| C | 6 | -1.413408 | 1.035368 | 0.760686 |
| C | 6 | -0.547134 | 1.016342 | 1.870879 |
| H | 1 | -2.411137 | 0.612581 | 0.824391 |
| H | 1 | -1.259018 | 1.733882 | -0.055399 |
| H | 1 | 0.193040 | -0.044950 | 1.551467 |
| H | 1 | -0.971012 | 0.712421 | 2.827617 |
| H | 1 | 0.190025 | 1.815175 | 1.939623 |
| C | 6 | 1.766656 | 0.494772 | -1.395646 |
| H | 1 | -0.053307 | 0.302657 | -2.494705 |
| H | 1 | 2.291048 | 1.073068 | -2.149232 |
| H | 1 | 2.293192 | 0.241299 | -0.481003 |

| | |
|---|---|
| Energy | -630.5498892 Hartree |
| ZPE | 0.1074648 Hartree/Molecule |
| Imaginary Frequency | -1130.27 $cm^{-1}$ |

Higher Energy Conformer-Vinyl substituent *anti* with sulfinyl substituent

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.0925789634 | .5751847788 | 2.5968672333 |
| S | 16.0 | -.7471995296 | .2303042937 | -.4663583460 |
| O | 8.0 | -.7286855617 | -.8928090991 | .6001483223 |
| C | 6.0 | 1.0633815340 | 1.2223783169 | .5742627346 |
| H | 1.0 | 2.1753953262 | -.3507121554 | 1.4705453768 |
| H | 1.0 | .2560180094 | -.5538409376 | 1.2760691292 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .1076320704 | -.4774899011 | -1.8393965043 |
| C | 6.0 | 1.2972901679 | .2674458152 | 1.5827247954 |
| H | 1.0 | .5749473970 | 2.1502512264 | .8121505141 |
| H | 1.0 | 1.6853078278 | 1.2666693892 | -.3020455010 |
| C | 6.0 | -.0157506041 | -.0272699728 | -3.0711579078 |
| H | 1.0 | .7504930990 | -1.3013047020 | -1.5801392110 |
| H | 1.0 | -.6807652705 | .7814061204 | -3.3218164410 |
| H | 1.0 | .5490956710 | -.4621036727 | -3.8757981942 |

Energy -628.3520410 Hartree
ZPE 0.115200 Hartree/Molecule
Imaginary Frequency -1788.93 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.0676020048 | .5487070073 | 2.5871520322 |
| S | 16.0 | -.7876476417 | .2479235651 | -.4730329094 |
| O | 8.0 | -.7497167407 | -.8926540078 | .6223929399 |
| C | 6.0 | 1.0906602939 | 1.2168895744 | .5613049908 |
| H | 1.0 | 2.1229253955 | -.4214529282 | 1.4568615770 |
| H | 1.0 | .2313376289 | -.5496757233 | 1.2837405313 |
| C | 6.0 | .1419963856 | -.4263795883 | -1.8108294139 |
| C | 6.0 | 1.2854851122 | .2573711006 | 1.5667710034 |
| H | 1.0 | .6359214106 | 2.1699652490 | .8005667910 |
| H | 1.0 | 1.7165324894 | 1.2271434062 | -.3225131678 |
| C | 6.0 | -.0388621649 | -.0376597582 | -3.0781719657 |
| H | 1.0 | .8843600124 | -1.1596469185 | -1.5169197742 |
| H | 1.0 | -.8003357524 | .6805255509 | -3.3507858285 |
| H | 1.0 | .5794806667 | -.4329470293 | -3.8704808059 |

Energy -629.2537953 Hartree
ZPE 0.110234 Hartree/Molecule
Imaginary Frequency -1112.79 $cm^{-1}$
CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) -629.3420115 Hartree

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1 | 3.220693 | -0.230750 | 0.019897 |
| S | 16 | -0.281451 | 0.585831 | -0.568734 |
| O | 8 | 0.660467 | 1.442009 | 0.367530 |
| C | 6 | 1.368304 | -1.203836 | -0.428404 |
| H | 1 | 2.318608 | -0.901426 | 1.464270 |
| H | 1 | 1.615537 | 0.617241 | 0.567283 |
| C | 6 | -1.466373 | -0.144350 | 0.544493 |
| C | 6 | 2.263726 | -0.544341 | 0.436090 |
| H | 1 | 1.559714 | -1.251979 | -1.495900 |
| H | 1 | 0.668371 | -1.945597 | -0.056580 |

| | | | | |
|---|---|---|---|---|
| C | 6 | -2.627206 | -0.658037 | 0.137305 |
| H | 1 | -1.147758 | -0.136206 | 1.584791 |
| H | 1 | -2.936842 | -0.636668 | -0.904247 |
| H | 1 | -3.309554 | -1.120594 | 0.843078 |

Energy -630.547821 Hartree
ZPE 0.107016 Hartree/Molecule
Imaginary Frequency -1153.75 $cm^{-1}$

**Ethenesulfenic acid**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -0.7510835511 | -0.0582652429 | -1.3005800641 |
| S | 16.0 | -0.8946899517 | -0.0718190004 | 0.3398579702 |
| C | 6.0 | 0.7857539125 | -0.0919817975 | 0.8532543109 |
| C | 6.0 | 1.8550838307 | -0.0286375531 | 0.0877041089 |
| H | 1.0 | 0.8604746229 | -0.1622448352 | 1.9264983356 |
| H | 1.0 | 1.7864576688 | 0.0573197340 | -0.9803593460 |
| H | 1.0 | 2.8357550143 | -0.0521273899 | 0.5268806818 |
| H | 1.0 | -0.7024106463 | -0.9498612150 | -1.6132440971 |

Energy -550.3849885 Hartree
ZPE 0.062154 Hartree/Molecule

MP2/6-31(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -0.7329325586 | -0.0323671445 | -1.3183690742 |
| S | 16.0 | -0.9043055741 | -0.0757590041 | 0.3585307504 |
| C | 6.0 | 0.7711195008 | -0.0933000746 | 0.8695355340 |
| C | 6.0 | 1.8470807958 | -0.0348307765 | 0.0764122703 |
| H | 1.0 | 0.8587719460 | -0.1585491373 | 1.9486688449 |
| H | 1.0 | 1.7510547997 | 0.0485662875 | -0.9951641519 |
| H | 1.0 | 2.8373238250 | -0.0560379693 | 0.5047829931 |
| H | 1.0 | -0.6527718345 | -0.9553394812 | -1.6043852664 |

Energy -550.9653003 Hartree
ZPE 0.058704 Hartree/Molecule
CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) -551.0238646 Hartree
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -551.2255750 Hartree

Becke3LYP/6-31(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8 | -0.766698 | 0.054855 | -1.342687 |
| S | 16 | -0.906777 | 0.003491 | 0.337724 |
| C | 6 | 0.780679 | -0.004399 | 0.852240 |
| C | 6 | 1.860244 | 0.050039 | 0.071324 |

| | | | | |
|---|---|---|---|---|
| H | 1 | 0.849406 | -0.062188 | 1.938025 |
| H | 1 | 1.777283 | 0.124357 | -1.007401 |
| H | 1 | 2.853560 | 0.034313 | 0.505982 |
| H | 1 | -0.683779 | -0.865021 | -1.640085 |

Energy -551.9811312 Hartree
ZPE 0.057351 Hartree/Molecule

**Ethyl Phenyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.5374382015 | -0.3465405685 | -1.4305746026 |
| S | 16.0 | -0.6493194537 | -0.7193012473 | -0.1390112499 |
| O | 8.0 | -0.9984476448 | -2.1597654926 | -0.2783561778 |
| C | 6.0 | 0.4304358392 | -0.5976012769 | 1.3122057997 |
| C | 6.0 | 1.5167972478 | -1.6628298837 | 1.3706713047 |
| H | 1.0 | -0.2463748423 | -0.6956993157 | 2.1544024072 |
| H | 1.0 | 0.8347694826 | 0.4087867682 | 1.3274715251 |
| H | 1.0 | 2.2526965194 | -1.5234082819 | 0.5878667398 |
| H | 1.0 | 1.0806778295 | -2.6474933832 | 1.2654866239 |
| H | 1.0 | 2.0259588957 | -1.6093986058 | 2.3274164108 |
| C | 6.0 | 2.3036293378 | 0.2173123192 | -3.4747703875 |
| C | 6.0 | 0.9587406029 | 0.9604629293 | -1.6324894243 |
| C | 6.0 | 0.9731898698 | -1.3685161743 | -2.2550142320 |
| C | 6.0 | 1.8621095257 | -1.0801692694 | -3.2797638732 |
| C | 6.0 | 1.8509011654 | 1.2389039633 | -2.6521187085 |
| H | 1.0 | 0.5906042763 | 1.7558687388 | -1.0069391546 |
| H | 1.0 | 0.6074974347 | -2.3642317079 | -2.0885734060 |
| H | 1.0 | 2.2055965278 | -1.8688891012 | -3.9251880156 |
| H | 1.0 | 2.1846127223 | 2.2487373102 | -2.8116212656 |
| H | 1.0 | 2.9924387624 | 0.4368483793 | -4.2711457136 |

Energy -781.1008905 Hartree
ZPE 0.173239 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.5130818233 | -0.3558636529 | -1.4060306838 |
| S | 16.0 | -0.7002822395 | -0.7588311354 | -0.1307333867 |
| O | 8.0 | -0.9924690382 | -2.2418024804 | -0.2532597346 |
| C | 6.0 | 0.4401264063 | -0.5655102289 | 1.2836140919 |
| C | 6.0 | 1.5163362815 | -1.6345814247 | 1.2965777882 |
| H | 1.0 | -0.1957812472 | -0.6395709794 | 2.1672601726 |
| H | 1.0 | 0.8423343134 | 0.4474308327 | 1.2346980675 |
| H | 1.0 | 2.2135272958 | -1.5009939311 | 0.4721018846 |
| H | 1.0 | 1.0535331343 | -2.6149747487 | 1.2023178942 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 2.0721052310 | -1.5960615216 | 2.2319958572 |
| C | 6.0 | 2.3242480008 | 0.2090439166 | -3.4310459230 |
| C | 6.0 | 0.9432381460 | 0.9603196316 | -1.5909737592 |
| C | 6.0 | 0.9548132892 | -1.3873811166 | -2.2316129295 |
| C | 6.0 | 1.8701607169 | -1.0984957266 | -3.2456253348 |
| C | 6.0 | 1.8603161444 | 1.2370808447 | -2.6049957823 |
| H | 1.0 | 0.5664438627 | 1.7588814388 | -0.9612401312 |
| H | 1.0 | 0.5721002522 | -2.3866050581 | -2.0636016897 |
| H | 1.0 | 2.2245755623 | -1.8913161591 | -3.8923969600 |
| H | 1.0 | 2.2043049301 | 2.2524347629 | -2.7567749911 |
| H | 1.0 | 3.0312394347 | 0.4298728360 | -4.2203198503 |

Energy -782.4998476 Hartree
ZPE 0.164595 Hartree/Molecule
CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) -782.6244001 Hartree
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -782.9993613 Hartree

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6 | -0.173338 | 0.275311 | -0.418432 |
| S | 16 | -1.398867 | -0.132256 | 0.873810 |
| O | 8 | -1.697722 | -1.613460 | 0.740464 |
| C | 6 | -0.277505 | 0.057192 | 2.346473 |
| C | 6 | 0.799285 | -1.016611 | 2.405282 |
| H | 1 | -0.957828 | -0.011443 | 3.201552 |
| H | 1 | 0.123134 | 1.075204 | 2.309460 |
| H | 1 | 1.542387 | -0.880228 | 1.615127 |
| H | 1 | 0.344521 | -2.003485 | 2.284824 |
| H | 1 | 1.312922 | -0.984042 | 3.371121 |
| C | 6 | 1.599872 | 0.846852 | -2.477302 |
| C | 6 | 0.269186 | 1.587883 | -0.597103 |
| C | 6 | 0.240101 | -0.748331 | -1.267406 |
| C | 6 | 1.134075 | -0.456922 | -2.299805 |
| C | 6 | 1.166787 | 1.868410 | -1.627382 |
| H | 1 | -0.081954 | 2.385890 | 0.052610 |
| H | 1 | -0.150314 | -1.748504 | -1.104228 |
| H | 1 | 1.464505 | -1.247886 | -2.966908 |
| H | 1 | 1.522448 | 2.884422 | -1.771544 |
| H | 1 | 2.293058 | 1.071159 | -3.282637 |

Energy -784.253976 Hartree
ZPE 0.161927 Hartree/Molecule

**Transition State for Ethyl Phenyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.0326275997 | 0.3384448063 | -1.5291317369 |
| S | 16.0 | -0.6194747245 | -0.6866237912 | -0.2298185524 |
| O | 8.0 | -0.8936175616 | 0.2839772080 | 0.9438987750 |
| C | 6.0 | -2.8719074204 | -0.5643898992 | -0.8164160443 |
| C | 6.0 | -3.2916051957 | 0.3947760956 | 0.1232351336 |
| H | 1.0 | -3.0960071265 | -1.6047783226 | -0.6643695316 |
| H | 1.0 | -2.6917837627 | -0.2921923465 | -1.8405260524 |
| H | 1.0 | -2.1033468645 | 0.5320847068 | 0.7614072674 |
| H | 1.0 | -3.9577926965 | 0.0521148159 | 0.9003679854 |
| H | 1.0 | -3.5129577544 | 1.3803530880 | -0.2566273862 |
| C | 6.0 | 1.0431470461 | 1.8729659362 | -3.5996490935 |
| C | 6.0 | 0.1950868821 | 1.7032392114 | -1.3544203513 |
| C | 6.0 | 0.3809789615 | -0.2645737926 | -2.7311156874 |
| C | 6.0 | 0.8831331547 | 0.5056282191 | -3.7647700413 |
| C | 6.0 | 0.7013077184 | 2.4654691929 | -2.3956077783 |
| H | 1.0 | -0.0632892221 | 2.1504140623 | -0.4138043714 |
| H | 1.0 | 0.2672460538 | -1.3280470388 | -2.8586217899 |
| H | 1.0 | 1.1522497528 | 0.0385125334 | -4.6954936414 |
| H | 1.0 | 0.8303987431 | 3.5250027666 | -2.2618993436 |
| H | 1.0 | 1.4362324166 | 2.4701770484 | -4.4029634596 |

| | |
|---|---|
| Energy | -781.0264047 Hartree |
| ZPE | 0.166824 Hartree/Molecule |
| Imaginary Frequency | -1794.55 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.0364443964 | 0.2855677973 | -1.4932209448 |
| S | 16.0 | -0.5766718251 | -0.7554554657 | -0.1871230377 |
| O | 8.0 | -0.8832880398 | 0.2500207217 | 0.9949091135 |
| C | 6.0 | -2.8253414460 | -0.5327370176 | -0.8690439697 |
| C | 6.0 | -3.2162017999 | 0.4519969943 | 0.0493858443 |
| H | 1.0 | -3.1253858347 | -1.5624118008 | -0.7185320245 |
| H | 1.0 | -2.5868738819 | -0.2703746188 | -1.8921017891 |
| H | 1.0 | -2.0577964715 | 0.5353126672 | 0.7583213102 |
| H | 1.0 | -3.9147025612 | 0.1667341146 | 0.8268385752 |
| H | 1.0 | -3.3298778331 | 1.4642388661 | -0.3193473631 |
| C | 6.0 | 0.9621699405 | 1.8736186761 | -3.5837517959 |
| C | 6.0 | 0.1409942512 | 1.6655849670 | -1.3131729266 |
| C | 6.0 | 0.3914722550 | -0.3092274841 | -2.7086783893 |
| C | 6.0 | 0.8573570750 | 0.4904119766 | -3.7516399931 |
| C | 6.0 | 0.6070428436 | 2.4555103150 | -2.3651995869 |
| H | 1.0 | -0.1249793612 | 2.0945519094 | -0.3562134303 |
| H | 1.0 | 0.3128697202 | -1.3832369272 | -2.8380815924 |
| H | 1.0 | 1.1353399371 | 0.0345615937 | -4.6934512317 |
| H | 1.0 | 0.6932874642 | 3.5265170036 | -2.2311715840 |
| H | 1.0 | 1.3247671710 | 2.4913702117 | -4.3950508841 |

| | |
|---|---|
| Energy | -782.4478313 Hartree |
| ZPE | 0.158125 Hartree/Molecule |
| Imaginary Frequency | -1116.07 $cm^{-1}$ |
| CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) | -782.5713797 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -782.9442778 Hartree |

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6 | 0.607925 | -0.120270 | -0.224145 |
| S | 16 | -0.027332 | -1.160288 | 1.098887 |
| O | 8 | -0.332709 | -0.166245 | 2.288644 |
| C | 6 | -2.396508 | -1.002058 | 0.502771 |
| C | 6 | -2.751764 | -0.048917 | 1.475193 |
| H | 1 | -2.613316 | -2.055145 | 0.652799 |
| H | 1 | -2.204447 | -0.712870 | -0.525554 |
| H | 1 | -1.566061 | 0.078137 | 2.086233 |
| H | 1 | -3.390127 | -0.382113 | 2.292959 |
| H | 1 | -2.954188 | 0.964664 | 1.130937 |
| C | 6 | 1.623719 | 1.439920 | -2.296978 |
| C | 6 | 0.740883 | 1.258239 | -0.048084 |
| C | 6 | 0.986336 | -0.726971 | -1.426670 |
| C | 6 | 1.493020 | 0.058992 | -2.461273 |
| C | 6 | 1.248394 | 2.034329 | -1.090624 |
| H | 1 | 0.458066 | 1.698773 | 0.902008 |
| H | 1 | 0.892914 | -1.802705 | -1.554887 |
| H | 1 | 1.788166 | -0.408839 | -3.396001 |
| H | 1 | 1.355020 | 3.107085 | -0.956908 |
| H | 1 | 2.020928 | 2.048011 | -3.104072 |

| | |
|---|---|
| Energy | -784.2122354 Hartree |
| ZPE | 0.155746 Hartree/Molecule |
| Imaginary Frequency | -1121.98 $cm^{-1}$ |

**Benzenesulfenic Acid**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.2322114133 | -0.5107765881 | -0.6048555469 |
| C | 6.0 | 0.1438808766 | -0.2773095671 | 1.1549245120 |
| C | 6.0 | -0.1137591067 | 0.0349903389 | 3.8993590961 |
| C | 6.0 | -0.0865843591 | -1.3821130983 | 1.9615676994 |
| C | 6.0 | 0.2496050741 | 0.9874839249 | 1.7221823206 |
| C | 6.0 | 0.1343664067 | 1.1359039999 | 3.0921451231 |
| C | 6.0 | -0.2304097557 | -1.2209060390 | 3.3311922748 |
| H | 1.0 | -0.1460986394 | -2.3637171357 | 1.5257450413 |
| H | 1.0 | 0.4285659794 | 1.8394796226 | 1.0932782899 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.2256011974 | 2.1142693249 | 3.5299601223 |
| H | 1.0 | -0.4152298636 | -2.0801977408 | 3.9511183069 |
| H | 1.0 | -0.2120096732 | 0.1575840224 | 4.9633031792 |
| O | 8.0 | 1.3992079494 | 0.5800258831 | -1.0272253678 |
| H | 1.0 | 2.2508467009 | 0.1839010524 | -0.9150940509 |

Energy -703.0559606 Hartree
ZPE 0.113470 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -0.0461867958 | -0.3612740114 | -0.6049121270 |
| C | 6.0 | -0.0281015120 | -0.1746100416 | 1.1571258266 |
| C | 6.0 | -0.1436019321 | 0.0773889288 | 3.9380518974 |
| C | 6.0 | -0.3590753629 | -1.2818036824 | 1.9473881856 |
| C | 6.0 | 0.2454093539 | 1.0600898146 | 1.7573210722 |
| C | 6.0 | 0.2073869944 | 1.1736068213 | 3.1462899054 |
| C | 6.0 | -0.4317789267 | -1.1475007499 | 3.3342368878 |
| H | 1.0 | -0.5458915771 | -2.2428023606 | 1.4829210077 |
| H | 1.0 | 0.5038368031 | 1.9076717353 | 1.1369718212 |
| H | 1.0 | 0.4310461322 | 2.1265874013 | 3.6092647491 |
| H | 1.0 | -0.6916001108 | -2.0054788523 | 3.9413223523 |
| H | 1.0 | -0.1837151368 | 0.1751484214 | 5.0151559400 |
| O | 8.0 | 1.1141098281 | 0.7820141974 | -1.0622227402 |
| H | 1.0 | 1.9734122425 | 0.3397923779 | -0.9865947780 |

Energy -704.1533510 Hartree
ZPE 0.106370 Hartree/Molecule
CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) -704.2480101 Hartree
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -704.5596355 Hartree

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16 | 0.104355 | -0.506041 | -1.905623 |
| C | 6 | -0.071173 | -0.197367 | -0.154315 |
| C | 6 | -0.438329 | 0.195870 | 2.588517 |
| C | 6 | -0.416058 | -1.278532 | 0.667423 |
| C | 6 | 0.092297 | 1.078788 | 0.393559 |
| C | 6 | -0.083580 | 1.265418 | 1.764931 |
| C | 6 | -0.608111 | -1.073853 | 2.032943 |
| H | 1 | -0.528191 | -2.274072 | 0.245949 |
| H | 1 | 0.355587 | 1.908158 | -0.253605 |
| H | 1 | 0.049846 | 2.256906 | 2.188598 |
| H | 1 | -0.877917 | -1.914491 | 2.665717 |
| H | 1 | -0.578612 | 0.348881 | 3.654128 |
| O | 8 | 0.901145 | 0.887710 | -2.432452 |
| H | 1 | 1.850163 | 0.727656 | -2.309568 |

| | |
|---|---|
| Energy | -705.6414382 Hartree |
| ZPE | 0.105736 Hartree/Molecule |

**Ethyl 1,1,1-Trifluoromethyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.6933159482 | -2.1598206068 | 1.4759193673 |
| H | 1.0 | -1.9790306043 | -1.0244536393 | 1.8779728818 |
| H | 1.0 | -0.6200963388 | -1.2358250830 | 2.9689847987 |
| S | 16.0 | -0.5713843174 | -0.0524283144 | -0.5257393752 |
| C | 6.0 | 0.5853663642 | 1.2774270385 | -1.0018379373 |
| O | 8.0 | -0.0480897852 | -1.2886118880 | -1.1412067041 |
| C | 6.0 | -0.1290742733 | -0.0895488787 | 1.2243935662 |
| H | 1.0 | 0.9371814717 | -0.2669425058 | 1.2854468419 |
| C | 6.0 | -0.9091988212 | -1.1989070022 | 1.9252532339 |
| H | 1.0 | -0.3570356907 | 0.8850509726 | 1.6396954497 |
| F | 9.0 | 1.8332943936 | 0.9928629268 | -0.7170507046 |
| F | 9.0 | 0.2548214082 | 2.3876255595 | -0.3696931055 |
| F | 9.0 | 0.4866455415 | 1.4860331208 | -2.2915248132 |

| | |
|---|---|
| Energy | -887.1453035 Hartree |
| ZPE | 0.092428 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -.1186844401 | -1.3473759683 | -1.1090321716 |
| S | 16.0 | -.6252441083 | -.0507959257 | -.5366050557 |
| C | 6.0 | .6024112103 | 1.2625622383 | -.9916861495 |
| F | 9.0 | 1.8655255367 | .9002722898 | -.7228951777 |
| F | 9.0 | .3189499807 | 2.3932024753 | -.3123059839 |
| F | 9.0 | .5011154890 | 1.5142551890 | -2.3043110939 |
| C | 6.0 | -.1925894388 | -.0214019214 | 1.2289737890 |
| C | 6.0 | -.8641941844 | -1.2052593979 | 1.9074496283 |
| H | 1.0 | -.5270832792 | .9349865160 | 1.6306370749 |
| H | 1.0 | .8920086353 | -.0878832072 | 1.3055848396 |
| H | 1.0 | -.5367088893 | -2.1343169913 | 1.4469712002 |
| H | 1.0 | -1.9491550171 | -1.1438258820 | 1.8321590432 |
| H | 1.0 | -.5961144809 | -1.2247015617 | 2.9615133665 |

| | |
|---|---|
| Energy | -888.3902636 Hartree |
| ZPE | 0.088203 Hartree/Molecule |
| CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) | -888.4677400 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -889.0919158 Hartree |

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1 | -0.731247 | -2.553811 | 1.818786 |
| H | 1 | -2.074021 | -1.480121 | 2.262018 |
| H | 1 | -0.680311 | -1.647068 | 3.341195 |
| S | 16 | -0.725345 | -0.455027 | -0.198957 |
| C | 6 | 0.500703 | 0.907360 | -0.654413 |
| O | 8 | -0.218213 | -1.739860 | -0.797952 |
| C | 6 | -0.268996 | -0.451756 | 1.594142 |
| H | 1 | 0.817611 | -0.561666 | 1.644042 |
| C | 6 | -0.986705 | -1.602597 | 2.292373 |
| H | 1 | -0.552973 | 0.528272 | 1.989382 |
| F | 9 | 1.764628 | 0.594214 | -0.346880 |
| F | 9 | 0.159667 | 2.034925 | -0.003675 |
| F | 9 | 0.420390 | 1.125934 | -1.969567 |

Energy -890.2137745 Hartree
ZPE 0.085539 Hartree/Molecule

**Transition State for Ethyl 1,1,1-Trifluoromethyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.0575841752 | -0.6718262871 | -1.7866064216 |
| S | 16.0 | -0.9054461055 | 0.0257959273 | -0.3502854443 |
| O | 8.0 | -0.6542078196 | -1.0287410796 | 0.7408763044 |
| C | 6.0 | 0.9593995550 | 1.2647168869 | 0.4733290193 |
| F | 9.0 | -0.7107982013 | -1.6816321888 | -2.3110439450 |
| F | 9.0 | 1.1569727186 | -1.0865113649 | -1.4960393046 |
| F | 9.0 | 0.0364768035 | 0.2776154894 | -2.7015615423 |
| C | 6.0 | 1.3382784251 | 0.3692881382 | 1.4875160082 |
| H | 1.0 | 0.3911701454 | 2.1468067174 | 0.7035211676 |
| H | 1.0 | 1.4854581282 | 1.3007997431 | -0.4621896294 |
| H | 1.0 | 1.1842386882 | 0.7030770974 | 2.5024604349 |
| H | 1.0 | 2.2516094745 | -0.1816401283 | 1.3240354989 |
| H | 1.0 | 0.3949570631 | -0.5278947507 | 1.3132422537 |

Energy -887.0734131 Hartree
ZPE 0.086218 Hartree/Molecule
Imaginary Frequency -1697.50 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.0290392994 | -0.6478244172 | -1.7350198398 |
| S | 16.0 | -0.9569955863 | 0.0121378977 | -0.3078180778 |
| O | 8.0 | -0.6533686898 | -1.0486511535 | 0.8082926674 |
| C | 6.0 | 0.9196498672 | 1.2536693400 | 0.4219293918 |
| F | 9.0 | -0.6869091618 | -1.6393332198 | -2.3552870461 |

| | | | | |
|---|---|---|---|---|
| F | 9.0 | 1.1735200606 | -1.1179229817 | -1.3674188150 |
| F | 9.0 | 0.1447059575 | 0.3565442110 | -2.6199763811 |
| C | 6.0 | 1.3364092301 | 0.3710651073 | 1.4295928539 |
| H | 1.0 | 0.3783038771 | 2.1556648916 | 0.6766799536 |
| H | 1.0 | 1.4264356540 | 1.2853452311 | -0.5326592809 |
| H | 1.0 | 1.2148062868 | 0.6963006756 | 2.4557140894 |
| H | 1.0 | 2.2237295711 | -0.2186498831 | 1.2346736859 |
| H | 1.0 | 0.3792769330 | -0.5484914988 | 1.3285511985 |

| | |
|---|---|
| Energy | -888.3408328 Hartree |
| ZPE | 0.082468 Hartree/Molecule |
| Imaginary Frequency | -1087.25 $cm^{-1}$ |
| CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) | -888.4180348 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -889.0370750 Hartree |

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6 | -0.100596 | -0.390815 | -1.102000 |
| S | 16 | -1.010671 | 0.285860 | 0.365668 |
| O | 8 | -0.704995 | -0.757799 | 1.498588 |
| C | 6 | 0.932184 | 1.577406 | 1.161384 |
| F | 9 | -0.757018 | -1.399464 | -1.686116 |
| F | 9 | 1.121405 | -0.828682 | -0.767723 |
| F | 9 | 0.020506 | 0.608839 | -1.996698 |
| C | 6 | 1.305762 | 0.672000 | 2.171469 |
| H | 1 | 0.361195 | 2.470195 | 1.395773 |
| H | 1 | 1.436363 | 1.593349 | 0.201177 |
| H | 1 | 1.162798 | 0.993353 | 3.202685 |
| H | 1 | 2.206641 | 0.083863 | 2.000231 |
| H | 1 | 0.355580 | -0.229917 | 2.030461 |

| | |
|---|---|
| Energy | -890.1729329 Hartree |
| ZPE | 0.079687 Hartree/Molecule |
| Imaginary Frequency | -1082.71 $cm^{-1}$ |

**1,1,1-Trifluoromethanesulfenic Acid**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -0.0590265432 | 0.1043921515 | -1.1916646322 |
| C | 6.0 | -0.1712598287 | 0.2177160032 | 0.5957452072 |
| F | 9.0 | 1.0170575168 | 0.2121343252 | 1.1675989509 |
| F | 9.0 | -0.8648957907 | -0.7582551428 | 1.1334024957 |
| F | 9.0 | -0.7669077626 | 1.3584659359 | 0.8780042617 |
| O | 8.0 | 0.7629941979 | -1.3100767675 | -1.2945990939 |
| H | 1.0 | 1.6938430106 | -1.1418795056 | -1.2589933894 |

| | |
|---|---|
| Energy | -809.1070235 Hartree |
| ZPE | 0.033039 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -0.0678150086 | 0.1179611300 | -1.2039120941 |
| C | 6.0 | -0.1721141903 | 0.2186716540 | 0.5894995539 |
| F | 9.0 | 1.0462788726 | 0.2070600133 | 1.1693773244 |
| F | 9.0 | -0.8779656718 | -0.7803000209 | 1.1404157662 |
| F | 9.0 | -0.7781793252 | 1.3858359041 | 0.8832925373 |
| O | 8.0 | 0.7589394370 | -1.3394659888 | -1.3079602260 |
| H | 1.0 | 1.7026606864 | -1.1272656919 | -1.2412190618 |

| | |
|---|---|
| Energy | -810.0517876 Hartree |
| ZPE | 0.030290 Hartree/Molecule |
| CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) | -810.0984880 Hartree |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -810.6600798 Hartree |

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16 | -0.051801 | 0.137761 | -1.232296 |
| C | 6 | -0.177126 | 0.245497 | 0.585944 |
| F | 9 | 1.030231 | 0.252533 | 1.179126 |
| F | 9 | -0.878221 | -0.756900 | 1.126867 |
| F | 9 | -0.800104 | 1.405666 | 0.854900 |
| O | 8 | 0.752724 | -1.331220 | -1.366496 |
| H | 1 | 1.702631 | -1.139088 | -1.314989 |

| | |
|---|---|
| Energy | -811.6041221 Hartree |
| ZPE | 0.029584 Hartree/Molecule |

**Di-t-butyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.7524338591 | 2.6119571282 | 0.6405494261 |
| C | 6.0 | 0.1895503185 | 1.5325733341 | 0.0734189642 |
| C | 6.0 | 0.4965930895 | 1.8623065918 | -1.3890486784 |
| S | 16.0 | -0.8540568104 | 0.0021588600 | 0.2272008030 |
| C | 6.0 | 1.4589761881 | 1.4737351392 | 0.9238174839 |
| H | 1.0 | 2.2152532841 | 0.8318527114 | 0.4905712938 |
| H | 1.0 | 1.8806737686 | 2.4722925509 | 0.9863059787 |
| H | 1.0 | 1.2562818829 | 1.1407508378 | 1.9369212894 |
| H | 1.0 | -1.6830532175 | 2.6430162355 | 0.0874752533 |
| H | 1.0 | -0.2728471979 | 3.5824833137 | 0.5604186768 |
| H | 1.0 | -0.9783203952 | 2.4326277487 | 1.6866464736 |
| H | 1.0 | 1.2683600072 | 1.2277520855 | -1.8023645124 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.3952780916 | 1.7636243420 | -1.9925010728 |
| H | 1.0 | 0.8479209357 | 2.8884567203 | -1.4511231360 |
| O | 8.0 | -1.8231469834 | 0.1122133049 | -0.9108861983 |
| C | 6.0 | 0.1231637569 | -1.5336062568 | -0.1219011377 |
| C | 6.0 | 0.8811012567 | -1.4861391588 | -1.4483507763 |
| C | 6.0 | -0.9772805090 | -2.6081167812 | -0.2078958859 |
| C | 6.0 | 1.0440676367 | -1.8662455228 | 1.0569569377 |
| H | 1.0 | -1.6604240904 | -2.4017096701 | -1.0194524333 |
| H | 1.0 | -1.5483665962 | -2.6663861951 | 0.7137192336 |
| H | 1.0 | -0.5105625252 | -3.5741828854 | -0.3737841645 |
| H | 1.0 | 0.2398844916 | -1.1201173024 | -2.2405105282 |
| H | 1.0 | 1.7664455922 | -0.8647564497 | -1.3918608194 |
| H | 1.0 | 1.2049611577 | -2.4893183483 | -1.7108891007 |
| H | 1.0 | 1.4164659891 | -2.8785002806 | 0.9331312787 |
| H | 1.0 | 1.9020509828 | -1.2121483230 | 1.1210477367 |
| H | 1.0 | 0.5097795366 | -1.8254217266 | 2.0008452074 |

Energy -785.7635230 Hartree
ZPE 0.266288 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.7266861286 | 2.6025581333 | 0.6376544850 |
| C | 6.0 | 0.1994587917 | 1.5199437619 | 0.0696004701 |
| C | 6.0 | 0.4792794365 | 1.8243553256 | -1.3950386189 |
| S | 16.0 | -0.8841414884 | 0.0034271806 | 0.2375493803 |
| C | 6.0 | 1.4634725792 | 1.4289980756 | 0.9103912874 |
| H | 1.0 | 2.2103308756 | 0.7813008790 | 0.4561627687 |
| H | 1.0 | 1.8987022564 | 2.4264781109 | 0.9940914549 |
| H | 1.0 | 1.2537276704 | 1.0750532145 | 1.9209959992 |
| H | 1.0 | -1.6579615399 | 2.6397184151 | 0.0739113184 |
| H | 1.0 | -0.2320377490 | 3.5714972172 | 0.5606616226 |
| H | 1.0 | -0.9592903883 | 2.4159036529 | 1.6863415935 |
| H | 1.0 | 1.2937703052 | 1.2254881106 | -1.7930713607 |
| H | 1.0 | -0.4193160949 | 1.6378662852 | -1.9826852935 |
| H | 1.0 | 0.7528663901 | 2.8758132956 | -1.4944260828 |
| O | 8.0 | -1.8492354990 | 0.1078035334 | -0.9385213979 |
| C | 6.0 | 0.1323390422 | -1.5192158028 | -0.1081190955 |
| C | 6.0 | 0.8837928624 | -1.4336373000 | -1.4269864124 |
| C | 6.0 | -0.9586507902 | -2.5905107391 | -0.2182964047 |
| C | 6.0 | 1.0359145629 | -1.8424150454 | 1.0767568998 |
| H | 1.0 | -1.6366861578 | -2.3631563603 | -1.0373619537 |
| H | 1.0 | -1.5390766724 | -2.6594117764 | 0.7028902371 |
| H | 1.0 | -0.4840052096 | -3.5561495493 | -0.3963071768 |
| H | 1.0 | 0.2271694688 | -1.0343605951 | -2.1996726504 |
| H | 1.0 | 1.7744056780 | -0.8127234712 | -1.3519577855 |
| H | 1.0 | 1.1990251069 | -2.4341597466 | -1.7289526621 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.4021209367 | -2.8643461900 | 0.9649154482 |
| H | 1.0 | 1.8997529262 | -1.1873222327 | 1.1399842156 |
| H | 1.0 | 0.4867184280 | -1.7876443792 | 2.0179473068 |

| | |
|---|---|
| Energy | -787.2678987 Hartree |
| ZPE | 0.257128 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -787.7815076 Hartree |

**Transition State for Di-t-butyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.5897194685 | -1.4918688654 | -1.1033791518 |
| C | 6.0 | 1.5138467108 | -0.0890554409 | -1.3083842742 |
| S | 16.0 | -0.8100709064 | 0.1010696073 | -0.4206150686 |
| C | 6.0 | 1.1410162470 | 0.3994030744 | -2.6853810102 |
| C | 6.0 | 2.3310343749 | 0.8693730260 | -0.4872300253 |
| H | 1.0 | 0.3693544175 | -1.7302345158 | -0.7795096232 |
| H | 1.0 | 2.2415221160 | -1.8189924242 | -0.3057671913 |
| H | 1.0 | 1.6819943272 | -2.0801971429 | -2.0070289697 |
| H | 1.0 | 0.3929900283 | -0.2378173761 | -3.1395717861 |
| H | 1.0 | 2.0357705795 | 0.3623858937 | -3.3054025860 |
| H | 1.0 | 0.7793269780 | 1.4195697142 | -2.6742975440 |
| H | 1.0 | 1.9016340643 | 1.8628922653 | -0.4681057588 |
| H | 1.0 | 3.3107774475 | 0.9430193247 | -0.9589350416 |
| H | 1.0 | 2.4809752769 | 0.5191044238 | 0.5235423933 |
| O | 8.0 | -0.9048066438 | -1.4469417847 | -0.5700604739 |
| C | 6.0 | -0.9700019185 | 0.3736775318 | 1.3918555135 |
| C | 6.0 | -2.4144908242 | 0.0145707072 | 1.7680773993 |
| C | 6.0 | -0.7080542763 | 1.8592349094 | 1.6561831756 |
| C | 6.0 | -0.0048625431 | -0.5163165633 | 2.1764710368 |
| H | 1.0 | -2.5626152359 | 0.1467207168 | 2.8372193968 |
| H | 1.0 | -2.6273932216 | -1.0167913305 | 1.5153745812 |
| H | 1.0 | -3.1250996156 | 0.6464823136 | 1.2461128650 |
| H | 1.0 | 1.0292188381 | -0.2437517310 | 2.0045187856 |
| H | 1.0 | -0.1378089622 | -1.5548376887 | 1.9020894962 |
| H | 1.0 | -0.1996232125 | -0.4168887734 | 3.2411193221 |
| H | 1.0 | 0.3196674295 | 2.1333826960 | 1.4446565561 |
| H | 1.0 | -0.9015878598 | 2.0838821348 | 2.7008361366 |
| H | 1.0 | -1.3591362843 | 2.4893279981 | 1.0574832465 |

| | |
|---|---|
| Energy | -785.7012332 Hartree |
| ZPE | 0.259019 Hartree/Molecule |
| Imaginary Frequency | -1573.16 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.5688611023 | -1.4631955272 | -1.0216030656 |
| C | 6.0 | 1.4442964696 | -0.0755242445 | -1.2329026001 |
| S | 16.0 | -0.8240570759 | 0.1245074644 | -0.4726492104 |
| C | 6.0 | 1.1319986593 | 0.3733111561 | -2.6409262925 |
| C | 6.0 | 2.2491375508 | 0.9152465946 | -0.4370584678 |
| H | 1.0 | 0.2849664854 | -1.7373302716 | -0.7396159712 |
| H | 1.0 | 2.1623572807 | -1.7874274006 | -0.1730534000 |
| H | 1.0 | 1.6586246195 | -2.0924055844 | -1.9019941044 |
| H | 1.0 | 0.4151582298 | -0.2974065073 | -3.1149734834 |
| H | 1.0 | 2.0485927025 | 0.3641719450 | -3.2374228843 |
| H | 1.0 | 0.7252187199 | 1.3843971095 | -2.6637373620 |
| H | 1.0 | 1.7745091138 | 1.8967516315 | -0.4106558589 |
| H | 1.0 | 3.2247939252 | 1.0408231069 | -0.9167858643 |
| H | 1.0 | 2.4292575356 | 0.5817562080 | 0.5825280033 |
| O | 8.0 | -0.9210074432 | -1.4563128369 | -0.6050914715 |
| C | 6.0 | -0.9312155002 | 0.3732764360 | 1.3519984687 |
| C | 6.0 | -2.3676772101 | 0.0272390639 | 1.7435753136 |
| C | 6.0 | -0.6383003797 | 1.8448790401 | 1.6214697685 |
| C | 6.0 | 0.0345730880 | -0.5522462164 | 2.0775825032 |
| H | 1.0 | -2.4909539302 | 0.1438913853 | 2.8222977815 |
| H | 1.0 | -2.5920571407 | -1.0032767702 | 1.4732048109 |
| H | 1.0 | -3.0802523616 | 0.6809150761 | 1.2409126801 |
| H | 1.0 | 1.0711425404 | -0.2862438149 | 1.8865204954 |
| H | 1.0 | -0.1273352214 | -1.5819135652 | 1.7625975344 |
| H | 1.0 | -0.1424847948 | -0.4870117701 | 3.1524379135 |
| H | 1.0 | 0.4001020331 | 2.0936299857 | 1.4116530098 |
| H | 1.0 | -0.8345437214 | 2.0636937077 | 2.6720847363 |
| H | 1.0 | -1.2804084770 | 2.4922072986 | 1.0214784170 |

| | |
|---|---|
| Energy | -787.2227484 Hartree |
| ZPE | 0.250408 Hartree/Molecule |
| Imaginary Frequency | -1114.06 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -787.7311766 Hartree |

**2-Methylpropanesulfenic Acid**

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.1718958272 | -0.8758513896 | -0.9737425390 |
| C | 6.0 | 0.0886315167 | 0.1478132529 | -0.6212895705 |
| C | 6.0 | 0.7049768323 | 1.5374922080 | -0.4372387508 |
| S | 16.0 | -0.7936703167 | -0.3729919681 | 0.8959100297 |
| C | 6.0 | -0.9953438630 | 0.1833266872 | -1.7061418870 |
| H | 1.0 | 1.8934779511 | -0.9667856438 | -0.1708110173 |
| H | 1.0 | 1.6990822334 | -0.5643285343 | -1.8721397717 |
| H | 1.0 | 0.7391608562 | -1.8535339884 | -1.1530027553 |
| H | 1.0 | -1.7743775567 | 0.9009117244 | -1.4690594682 |
| H | 1.0 | -1.4549812505 | -0.7905264574 | -1.8402785241 |
| H | 1.0 | -0.5498643046 | 0.4744832686 | -2.6523073577 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.4444053562 | 1.5346481658 | 0.3563126161 |
| H | 1.0 | -0.0535031569 | 2.2759436447 | -0.2007720956 |
| H | 1.0 | 1.2070973673 | 1.8458274913 | -1.3505170045 |
| O | 8.0 | 0.4380337800 | -0.4031927226 | 2.0050917851 |
| H | 1.0 | 0.4601260039 | 0.4229091464 | 2.4628657098 |

Energy -629.6577677 Hartree
ZPE 0.146529 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .9638240695 | -1.2871288122 | -.7503342251 |
| C | 6.0 | .0773944631 | -.0527649947 | -.6208205389 |
| C | 6.0 | .9256231109 | 1.2142713014 | -.6004161262 |
| S | 16.0 | -.9179730369 | -.1708986620 | .9028799937 |
| C | 6.0 | -.9524923998 | .0042219992 | -1.7478346178 |
| H | 1.0 | 1.6165578782 | -1.3757610196 | .1165540058 |
| H | 1.0 | 1.5823203941 | -1.2089677010 | -1.6465840487 |
| H | 1.0 | .3597848432 | -2.1905378166 | -.8208481311 |
| H | 1.0 | -1.5956058020 | .8797943696 | -1.6549487783 |
| H | 1.0 | -1.5776325743 | -.8889565361 | -1.7582692053 |
| H | 1.0 | -.4322398428 | .0644640394 | -2.7042586364 |
| H | 1.0 | 1.6157841506 | 1.1977645894 | .2427368116 |
| H | 1.0 | .2992849549 | 2.1027681005 | -.5259623746 |
| H | 1.0 | 1.5175107930 | 1.2819189761 | -1.5148105838 |
| O | 8.0 | .3115340868 | -.2417760045 | 2.0719462257 |
| H | 1.0 | .4583838354 | .6715881716 | 2.3580191453 |

Energy -630.5598493 Hartree
ZPE 0.141467 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -630.9003997 Hartree

**t-Butyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.0138142851 | -0.0169765645 | -0.3997433171 |
| C | 6.0 | -0.0021246394 | 0.0165276373 | 1.1360896058 |
| C | 6.0 | 1.4398417606 | -0.0318329393 | 1.6445123168 |
| S | 16.0 | -0.9195306827 | -1.5026225498 | 1.6244595250 |
| C | 6.0 | -0.7493157180 | 1.2541328359 | 1.6414247853 |
| H | 1.0 | -0.3038689875 | 2.1419888461 | 1.2040753603 |
| H | 1.0 | -0.6902581496 | 1.3601372336 | 2.7187679986 |
| H | 1.0 | -1.7963037003 | 1.2353889158 | 1.3534766153 |
| H | 1.0 | 0.4643983049 | -0.9154568244 | -0.7688721162 |
| H | 1.0 | 0.5228053698 | 0.8445472678 | -0.7842695376 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.0271744714 | 0.0174137737 | -0.7881196586 |
| H | 1.0 | 2.0152313928 | 0.7605770008 | 1.1751148392 |
| H | 1.0 | 1.8957031016 | -0.9822179885 | 1.3969208101 |
| H | 1.0 | 1.5000874663 | 0.1160221087 | 2.7171559578 |
| O | 8.0 | -0.0635124033 | -2.6554509886 | 1.2217420566 |
| S | 6.0 | -0.8356468995 | -1.4471548966 | 3.4179445456 |
| H | 1.0 | 0.1927099624 | -1.4619828840 | 3.7509753209 |
| H | 1.0 | -1.3264637820 | -2.3482051420 | 3.7620480589 |
| H | 1.0 | -1.3606074317 | -0.5848900269 | 3.8062974813 |

Energy -668.6609784 Hartree
ZPE 0.175525 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.0070123409 | -0.0032380100 | -0.3904892821 |
| C | 6.0 | -0.0049140482 | 0.0261109119 | 1.1379696724 |
| C | 6.0 | 1.4235777150 | -0.0495345757 | 1.6561321471 |
| S | 16.0 | -0.9239975024 | -1.5154538707 | 1.5952143333 |
| C | 6.0 | -0.7629338559 | 1.2424609768 | 1.6530974921 |
| H | 1.0 | -0.3365646345 | 2.1425765855 | 1.2085711227 |
| H | 1.0 | -0.6922794159 | 1.3436837792 | 2.7350126025 |
| H | 1.0 | -1.8173084280 | 1.2015899007 | 1.3734647241 |
| H | 1.0 | 0.4751566780 | -0.9099974917 | -0.7520242484 |
| H | 1.0 | 0.5372592321 | 0.8616625111 | -0.7704082822 |
| H | 1.0 | -1.0241645033 | 0.0313442566 | -0.7832043677 |
| H | 1.0 | 2.0344491558 | 0.7046366169 | 1.1588588506 |
| H | 1.0 | 1.8381839555 | -1.0341432969 | 1.4375166544 |
| H | 1.0 | 1.4809302870 | 0.1309421329 | 2.7288704140 |
| O | 8.0 | -0.0378486940 | -2.6771775500 | 1.1848168853 |
| S | 6.0 | -0.8187218102 | -1.4171606340 | 3.3982709071 |
| H | 1.0 | 0.2224247318 | -1.4204184950 | 3.7106646276 |
| H | 1.0 | -1.3021095586 | -2.3164540778 | 3.7729389498 |
| H | 1.0 | -1.3419707554 | -0.5414848548 | 3.7747274454 |

Energy -669.7183434 Hartree
ZPE 0.169569 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -670.1150529 Hartree

**Transition State for *t*-Butyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.3812445448 | -1.1248770084 | -0.0940252244 |
| C | 6.0 | 1.0403232419 | 0.1802998082 | -0.5339308485 |
| S | 16.0 | -1.2958153880 | 0.0170928970 | 0.0601935188 |
| C | 6.0 | 0.8491475171 | 0.4060721444 | -2.0146379696 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.4924350779 | 1.3882692406 | 0.2455439103 |
| H | 1.0 | 0.1743022958 | -1.5743111001 | 0.1987090970 |
| H | 1.0 | 1.9788239624 | -1.1832802700 | 0.8047690126 |
| H | 1.0 | 1.6937012104 | -1.8119722051 | -0.8683357484 |
| H | 1.0 | 0.3516961946 | -0.4358612942 | -2.4797739885 |
| H | 1.0 | 1.8317476004 | 0.5090708846 | -2.4719116679 |
| H | 1.0 | 0.2845200318 | 1.3067789151 | -2.2219899974 |
| H | 1.0 | 0.8811938551 | 2.2606541126 | 0.0447031110 |
| H | 1.0 | 2.5104090997 | 1.6211676963 | -0.0627855163 |
| H | 1.0 | 1.5101614625 | 1.2014084609 | 1.3111623934 |
| O | 8.0 | -1.0984608008 | -1.5060891379 | 0.2987322537 |
| C | 6.0 | -1.3748128257 | 0.6839084780 | 1.7275671955 |
| H | 1.0 | -2.2713071124 | 0.3183352046 | 2.2105951986 |
| H | 1.0 | -1.4115555005 | 1.7659987591 | 1.6742635168 |
| H | 1.0 | -0.5122007670 | 0.3709326145 | 2.3019876535 |

| | |
|---|---|
| Energy | -668.5911009 Hartree |
| ZPE | 0.168909 Hartree/Molecule |
| Imaginary Frequency | -1697.42 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.3658850984 | -1.1071961471 | -0.0711012051 |
| C | 6.0 | 1.0075430828 | 0.1827838984 | -0.5085424146 |
| S | 16.0 | -1.2948188920 | 0.0441388007 | 0.0050529736 |
| C | 6.0 | 0.8555945229 | 0.3993146363 | -1.9949030963 |
| C | 6.0 | 1.4625666834 | 1.3960591549 | 0.2583162731 |
| H | 1.0 | 0.1150159053 | -1.5875865630 | 0.1882488022 |
| H | 1.0 | 1.9091095553 | -1.1863435490 | 0.8647505865 |
| H | 1.0 | 1.6609997879 | -1.8283283482 | -0.8263137089 |
| H | 1.0 | 0.3721560402 | -0.4563723177 | -2.4664321499 |
| H | 1.0 | 1.8412203901 | 0.5229874934 | -2.4512302484 |
| H | 1.0 | 0.2676592377 | 1.2903871827 | -2.2160908265 |
| H | 1.0 | 0.8117015013 | 2.2558007730 | 0.0883349133 |
| H | 1.0 | 2.4651724160 | 1.6757875394 | -0.0764522481 |
| H | 1.0 | 1.5186316681 | 1.2058244608 | 1.3293346786 |
| O | 8.0 | -1.1064924411 | -1.5139698605 | 0.2374081918 |
| C | 6.0 | -1.3053738361 | 0.6798747612 | 1.6903122707 |
| H | 1.0 | -2.1751399019 | 0.2892652479 | 2.2120445124 |
| H | 1.0 | -1.3535438327 | 1.7673164046 | 1.6599272211 |
| H | 1.0 | -0.4023332856 | 0.3638546324 | 2.2081713750 |

| | |
|---|---|
| Energy | -669.6670055 Hartree |
| ZPE | 0.163162 Hartree/Molecule |
| Imaginary Frequency | -1109.83 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -670.0586325 Hartree |

**2-Methyl-1-propene (Isobutylene)**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.0213322949 | 0.0000160996 | -0.4047696864 |
| C | 6.0 | 0.0379609242 | -0.0000455162 | 1.1019340796 |
| C | 6.0 | 1.1819785321 | 0.0000133992 | 1.7624485222 |
| C | 6.0 | -1.2964758929 | 0.0000371315 | 1.8039114202 |
| H | 1.0 | 0.9683073605 | -0.0000011680 | -0.8458269342 |
| H | 1.0 | -0.5568085607 | 0.8737797501 | -0.7691644130 |
| H | 1.0 | -0.5568149050 | -0.8737832239 | -0.7691633115 |
| H | 1.0 | -1.1836636976 | -0.0000017890 | 2.8814894430 |
| H | 1.0 | -1.8798448992 | -0.8738016676 | 1.5223595478 |
| H | 1.0 | -1.8798307934 | 0.8737813265 | 1.5223723159 |
| H | 1.0 | 2.1297057493 | 0.0000046319 | 1.2520320460 |
| H | 1.0 | 1.2138373075 | 0.0000010259 | 2.8383338065 |

Energy -156.1238464 Hartree
ZPE 0.114964 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.0247720077 | 0.0000146889 | -0.4047930802 |
| C | 6.0 | 0.0293871540 | -0.0000188166 | 1.0969568078 |
| C | 6.0 | 1.1898909398 | 0.0000045472 | 1.7670060738 |
| C | 6.0 | -1.2982599060 | 0.0000047394 | 1.8009519314 |
| H | 1.0 | 0.9723633370 | -0.0000025437 | -0.8414390696 |
| H | 1.0 | -0.5610103819 | 0.8772662503 | -0.7720515315 |
| H | 1.0 | -0.5610152152 | -0.8772719153 | -0.7720575652 |
| H | 1.0 | -1.1778343280 | -0.0000003774 | 2.8828079076 |
| H | 1.0 | -1.8844354068 | -0.8772692341 | 1.5201778896 |
| H | 1.0 | -1.8844294332 | 0.8772676482 | 1.5201735249 |
| H | 1.0 | 2.1399381373 | 0.0000030736 | 1.2500013161 |
| H | 1.0 | 1.2171959405 | 0.0000019397 | 2.8482226314 |

Energy -156.6919247Hartree
ZPE 0.110695 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -156.8498071 Hartree

**Ethyl Hydrogen Sulfoxide (or Ethanesulfinyl Hydride or Ethane Thiol s-Oxide)**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.1325830597 | 0.1463821897 | -1.4965874114 |
| S | 16.0 | 0.1473855659 | -0.4900735404 | -0.3103494228 |

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 1.5277242493 | -0.4408148422 | 0.2320065328 |
| C | 6.0 | -0.8140325327 | 0.8019624403 | 0.5070474574 |
| C | 6.0 | -0.9984209261 | 0.4825488708 | 1.9863846002 |
| H | 1.0 | -1.7651825179 | 0.8629535096 | -0.0145499891 |
| H | 1.0 | -0.2818048602 | 1.7368164029 | 0.3780165487 |
| H | 1.0 | -0.0357926981 | 0.3846395411 | 2.4725779271 |
| H | 1.0 | -1.5502772851 | -0.4416487265 | 2.1250364543 |
| H | 1.0 | -1.5480856996 | 1.2812199966 | 2.4716435449 |

Energy -551.5363455 Hartree
ZPE 0.085448 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.1229434894 | 0.1880514825 | -1.4841135894 |
| S | 16.0 | 0.1462683209 | -0.5013597099 | -0.3035211722 |
| O | 8.0 | 1.5347274120 | -0.4721475261 | 0.2887781644 |
| C | 6.0 | -0.8286177835 | 0.8048969315 | 0.4998409790 |
| C | 6.0 | -0.9915281557 | 0.4841444525 | 1.9756029753 |
| H | 1.0 | -1.7855615790 | 0.8567955396 | -0.0245278313 |
| H | 1.0 | -0.2969685698 | 1.7460624022 | 0.3622740685 |
| H | 1.0 | -0.0130729180 | 0.3825450997 | 2.4403074405 |
| H | 1.0 | -1.5400883685 | -0.4463467863 | 2.1174774245 |
| H | 1.0 | -1.5340054925 | 1.2813439563 | 2.4791077827 |

Energy -552.1492748 Hartree
ZPE 0.082386 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -552.4273996 Hartree

**Transition State for Ethyl Hydrogen Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.4308089043 | 0.1894488058 | -1.3536234298 |
| S | 16.0 | -0.1158470132 | -0.6605489575 | -0.4776477124 |
| O | 8.0 | 0.8199798292 | -0.5754763688 | 0.7519294792 |
| C | 6.0 | -1.5186729311 | 0.9142796681 | 0.4916747019 |
| C | 6.0 | -0.7761053376 | 1.1645021363 | 1.6634205880 |
| H | 1.0 | -2.3930861887 | 0.2909024836 | 0.5257226851 |
| H | 1.0 | -1.5123796995 | 1.6161036544 | -0.3227192998 |
| H | 1.0 | 0.2213830047 | 0.2991172858 | 1.4346148951 |
| H | 1.0 | -1.2106893585 | 0.8177797387 | 2.5886975232 |
| H | 1.0 | -0.2908532837 | 2.1267149775 | 1.7285131626 |

Energy -551.4642603 Hartree
ZPE 0.079007 Hartree/Molecule
Imaginary Frequency -1758.79 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.3986062592 | 0.2146039691 | -1.3474693257 |
| S | 16.0 | -0.1017598702 | -0.6849312238 | -0.4738965100 |
| O | 8.0 | 0.8351622465 | -0.5596524563 | 0.7883035782 |
| C | 6.0 | -1.5254431224 | 0.9155222644 | 0.4792986264 |
| C | 6.0 | -0.7851276369 | 1.1609261347 | 1.6484517475 |
| H | 1.0 | -2.4133705260 | 0.2988627709 | 0.5208685141 |
| H | 1.0 | -1.5155804230 | 1.6295887822 | -0.3343049897 |
| H | 1.0 | 0.2227469837 | 0.3007893936 | 1.4487559061 |
| H | 1.0 | -1.1966243563 | 0.7987945343 | 2.5827241706 |
| H | 1.0 | -0.2640716287 | 2.1083192548 | 1.7178508756 |

| | |
|---|---|
| Energy | -552.0993379 Hartree |
| ZPE | 0.076017 Hartree/Molecule |
| Imaginary Frequency | -1099.49 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -552.3732026 Hartree |

**Hydrogen Sulfenic Acid (or Hydrogen Monothioperoxide)**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -0.2486020197 | -0.4842874227 | -1.2826566167 |
| S | 16.0 | -0.2460494616 | -0.3575766064 | 0.3654596040 |
| H | 1.0 | 0.4524684645 | 0.7677131048 | 0.4812283507 |
| H | 1.0 | -1.0236074213 | -0.0628487627 | -1.6211487180 |

| | |
|---|---|
| Energy | -473.4999919 Hartree |
| ZPE | 0.024735 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -0.2331303782 | -0.4948030466 | -1.3065744366 |
| S | 16.0 | -0.2533405275 | -0.3530225290 | 0.3793001846 |
| H | 1.0 | 0.4593879202 | 0.7717826777 | 0.4904781349 |
| H | 1.0 | -1.0387074525 | -0.0609567891 | -1.6203212629 |

| | |
|---|---|
| Energy | -473.8136596 Hartree |
| ZPE | 0.023267 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -473.9985333 Hartree |

**Ethyl Fluoro Sulfoxide (or Ethanesulfinyl Fluoride)**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| F | 9.0 | 0.1260271375 | 0.2366536063 | -1.7243386555 |

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.1166518674 | -0.5117789518 | -0.3040136465 |
| O | 8.0 | 1.4544765190 | -0.4422535529 | 0.2387515687 |
| C | 6.0 | -0.8203759527 | 0.7849136290 | 0.5009138749 |
| C | 6.0 | -0.9865308375 | 0.4877473912 | 1.9885124348 |
| H | 1.0 | -1.7742993422 | 0.8500366901 | -0.0105356783 |
| H | 1.0 | -0.2670005181 | 1.7012531783 | 0.3327409803 |
| H | 1.0 | -0.0226274310 | 0.4311136104 | 2.4782325781 |
| H | 1.0 | -1.5139825598 | -0.4466600545 | 2.1541687638 |
| H | 1.0 | -1.5620440286 | 1.2794419528 | 2.4532681026 |

Energy -650.4043751 Hartree
ZPE 0.078529 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| F | 9.0 | 0.1379984264 | 0.2998817840 | -1.7501987308 |
| S | 16.0 | 0.1084466836 | -0.5263725244 | -0.3024708457 |
| O | 8.0 | 1.4510955967 | -0.4834443743 | 0.3175446417 |
| C | 6.0 | -0.8388164576 | 0.7813586641 | 0.4958752917 |
| C | 6.0 | -0.9780674851 | 0.4912868885 | 1.9820255939 |
| H | 1.0 | -1.8010784899 | 0.8357502590 | -0.0135314558 |
| H | 1.0 | -0.2859784915 | 1.7016303930 | 0.3082831458 |
| H | 1.0 | 0.0027442143 | 0.4360600541 | 2.4485355130 |
| H | 1.0 | -1.4990550251 | -0.4493125182 | 2.1586227271 |
| H | 1.0 | -1.5469941178 | 1.2836288730 | 2.4630144420 |

Energy -651.1909559 Hartree
ZPE 0.075589 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -651.5964153 Hartree

**Transition State for Ethyl Fluoro Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| F | 9.0 | 0.5189323835 | 0.4100210353 | -1.5038560737 |
| S | 16.0 | -0.0890174212 | -0.6711777926 | -0.4796331424 |
| O | 8.0 | 0.7908453639 | -0.5731865115 | 0.7431216505 |
| C | 6.0 | -1.5336062498 | 0.9106387243 | 0.5088501800 |
| C | 6.0 | -0.7972834011 | 1.1780848368 | 1.6660740649 |
| H | 1.0 | -2.4152698115 | 0.2968110414 | 0.5475274643 |
| H | 1.0 | -1.4676161693 | 1.5551615456 | -0.3492435719 |
| H | 1.0 | 0.2157773028 | 0.2804508466 | 1.4150991738 |
| H | 1.0 | -1.2106672527 | 0.8449176583 | 2.6050963327 |
| H | 1.0 | -0.2626258516 | 2.1142961758 | 1.7046541769 |

Energy -650.3133267 Hartree
ZPE 0.072082 Hartree/Molecule

Imaginary Frequency -1803.71 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| F | 9.0 | 0.5034504887 | 0.4425730786 | -1.5352653210 |
| S | 16.0 | -0.0657201428 | -0.7003802222 | -0.4861911148 |
| O | 8.0 | 0.7999144716 | -0.5524090169 | 0.7915457169 |
| C | 6.0 | -1.5524636180 | 0.9195875068 | 0.5100280756 |
| C | 6.0 | -0.8235947706 | 1.1895565614 | 1.6627588085 |
| H | 1.0 | -2.4423533570 | 0.3057376708 | 0.5513460390 |
| H | 1.0 | -1.4584640824 | 1.5497340106 | -0.3643648280 |
| H | 1.0 | 0.2228290709 | 0.2593513973 | 1.4178801595 |
| H | 1.0 | -1.2048892217 | 0.8382436910 | 2.6129840575 |
| H | 1.0 | -0.2292399459 | 2.0940228825 | 1.6969686619 |

Energy -651.1182614 Hartree
ZPE 0.069045 Hartree/Molecule
Imaginary Frequency -1091.88 $cm^{-1}$
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -651.5218605 Hartree

**Fluorine Sulfenic Acid**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -0.2766316712 | -0.5219611471 | -1.2591615080 |
| S | 16.0 | -0.2261268863 | -0.3798231687 | 0.3433610741 |
| F | 9.0 | 0.5649797567 | 1.0086091584 | 0.4875733281 |
| H | 1.0 | -0.9974917002 | -0.0238285156 | -1.6187740172 |

Energy -572.3327060 Hartree
ZPE 0.018769 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -0.2701053173 | -0.5430896063 | -1.2876021201 |
| S | 16.0 | -0.2353632024 | -0.3778093830 | 0.3468234792 |
| F | 9.0 | 0.5895144488 | 1.0339088945 | 0.5222313395 |
| H | 1.0 | -1.0193164301 | -0.0300135782 | -1.6284538216 |

Energy -572.8158697 Hartree
ZPE 0.017427 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -573.1325720 Hartree

**Ethane Sulfinamide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| N | 7.0 | -0.1262932711 | -0.0703454498 | -1.8804552306 |
| S | 16.0 | -0.0439369219 | -0.6687006046 | -0.3147684906 |
| O | 8.0 | 1.3402812977 | -0.6140095636 | 0.1918268106 |
| C | 6.0 | -0.9030929359 | 0.7111220649 | 0.4557624379 |
| C | 6.0 | -0.9391374529 | 0.5494791588 | 1.9715409173 |
| H | 1.0 | -1.8960341937 | 0.7442547235 | 0.0242721271 |
| H | 1.0 | -0.3708319128 | 1.6150225520 | 0.1765376242 |
| H | 1.0 | 0.0649428179 | 0.4936821624 | 2.3722637743 |
| H | 1.0 | -1.4754818480 | -0.3490130052 | 2.2604441401 |
| H | 1.0 | -1.4440810413 | 1.3983005225 | 2.4191479912 |
| H | 1.0 | 0.4748985812 | 0.7236560591 | -2.0069358768 |
| H | 1.0 | 0.1210996807 | -0.7820243199 | -2.5389702248 |

Energy -606.5837731 Hartree
ZPE 0.104972 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| N | 7.0 | -0.1522093934 | -0.0523712128 | -1.8852970593 |
| S | 16.0 | -0.0692343488 | -0.7128020953 | -0.3050886397 |
| O | 8.0 | 1.3207508024 | -0.6892724099 | 0.2680551304 |
| C | 6.0 | -0.9285343378 | 0.6960894995 | 0.4407085591 |
| C | 6.0 | -0.9213406485 | 0.5608660024 | 1.9540980821 |
| H | 1.0 | -1.9337961355 | 0.7189065693 | 0.0222225937 |
| H | 1.0 | -0.3949450990 | 1.5966245644 | 0.1291534097 |
| H | 1.0 | 0.1020425858 | 0.4956653957 | 2.3159066581 |
| H | 1.0 | -1.4575436832 | -0.3321503701 | 2.2730101889 |
| H | 1.0 | -1.4012124195 | 1.4243387442 | 2.4102203768 |
| H | 1.0 | 0.4281126998 | 0.7832963030 | -1.9505478778 |
| H | 1.0 | 0.2102427775 | -0.7377666902 | -2.5417754223 |

Energy -607.3696941 Hartree
ZPE 0.100827 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -607.7129937 Hartree

**Transition State for Ethane Sulfinamide--Oxygen as base**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| N | 7.0 | 0.4859721696 | 0.4142096116 | -1.6671150693 |
| S | 16.0 | -0.1356597761 | -0.6234793338 | -0.5090294491 |
| O | 8.0 | 0.7938390663 | -0.5864520915 | 0.7187956971 |
| C | 6.0 | -1.5170409519 | 0.8873641577 | 0.4821866019 |
| C | 6.0 | -0.7680567253 | 1.1862492311 | 1.6363504739 |
| H | 1.0 | -2.3854208908 | 0.2573511684 | 0.5547807444 |
| H | 1.0 | -1.5478262117 | 1.5633309192 | -0.3553419897 |
| H | 1.0 | 0.2554337627 | 0.2628148695 | 1.3917512548 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.1799265061 | 0.8639009037 | 2.5800368174 |
| H | 1.0 | -0.2761785431 | 2.1467150728 | 1.6666706602 |
| H | 1.0 | 0.6777078479 | 1.3334558240 | -1.3201398121 |
| H | 1.0 | 1.3005438183 | 0.0402389252 | -2.1109784953 |

Energy -606.5020176 Hartree
ZPE 0.098859 Hartree/Molecule
Imaginary Frequency -1788.78 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| N | 7.0 | 0.4589569999 | 0.3931824487 | -1.6799372101 |
| S | 16.0 | -0.1121813501 | -0.6887908740 | -0.5093455236 |
| O | 8.0 | 0.8046506391 | -0.6033738834 | 0.7731991637 |
| C | 6.0 | -1.5167711483 | 0.9075626981 | 0.4674051803 |
| C | 6.0 | -0.7682887954 | 1.1867487566 | 1.6171401767 |
| H | 1.0 | -2.4057199211 | 0.2942940119 | 0.5375235281 |
| H | 1.0 | -1.5111473412 | 1.5796333768 | -0.3831666389 |
| H | 1.0 | 0.2463089923 | 0.2476739439 | 1.4071841982 |
| H | 1.0 | -1.1597011280 | 0.8555111146 | 2.5706940045 |
| H | 1.0 | -0.2064835662 | 2.1123157435 | 1.6492425585 |
| H | 1.0 | 0.5091342359 | 1.3491498886 | -1.3431290076 |
| H | 1.0 | 1.3646294429 | 0.1117920325 | -2.0388429956 |

Energy -607.3110859 Hartree
ZPE 0.094530 Hartree/Molecule
Imaginary Frequency -1131.70 $cm^{-1}$
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -607.6506773 Hartree

**Amino Sulfenic Acid**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -0.3475884340 | -0.6025060131 | -1.3584496217 |
| S | 16.0 | -0.2312657970 | -0.3423602035 | 0.2711441383 |
| N | 7.0 | 0.6240823287 | 1.0600736343 | 0.4425318530 |
| H | 1.0 | -1.1347958151 | -0.1983652363 | -1.6910831082 |
| H | 1.0 | 1.5798335264 | 1.0273560271 | 0.1591291712 |
| H | 1.0 | 0.1653739369 | 1.9048180105 | 0.1772871815 |

Energy -528.5331414 Hartree
ZPE 0.045384 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -0.3494909296 | -0.6364956441 | -1.3948852990 |
| S | 16.0 | -0.2299899116 | -0.3405406739 | 0.2745509685 |
| N | 7.0 | 0.6287329667 | 1.0686644582 | 0.4575707097 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.1625011345 | -0.2044514364 | -1.6953378221 |
| H | 1.0 | 1.5987273383 | 1.0368018833 | 0.1774812816 |
| H | 1.0 | 0.1701614167 | 1.9250376318 | 0.1811797753 |

| | |
|---|---|
| Energy | -529.0203190 Hartree |
| ZPE | 0.042789 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -529.2711990 Hartree |

**Transition State for Ethane Sulfinamide--Nitrogen as base**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| N | 7.0 | 0.4377956442 | -1.3632022797 | -0.3085163653 |
| S | 16.0 | -0.8446322515 | -0.1812865245 | -0.5572803108 |
| O | 8.0 | -1.6763531425 | -0.2871903063 | 0.6866798547 |
| C | 6.0 | 0.7421445088 | 1.4010381582 | 0.2897196055 |
| C | 6.0 | 1.8477506218 | 0.6499569890 | 0.6796288690 |
| H | 1.0 | -0.0406363817 | 1.6307159663 | 0.9900535635 |
| H | 1.0 | 0.7905423612 | 2.0355301295 | -0.5769207834 |
| H | 1.0 | 1.3088412886 | -0.6449677483 | 0.1861183117 |
| H | 1.0 | 1.9517946505 | 0.4206344927 | 1.7287914116 |
| H | 1.0 | 2.7726242488 | 0.7862167634 | 0.1405794273 |
| H | 1.0 | 0.7323213242 | -1.8184391788 | -1.1532670899 |
| H | 1.0 | 0.1122628276 | -2.0444657615 | 0.3562381061 |

| | |
|---|---|
| Energy | -606.4602975 Hartree |
| ZPE | 0.098403 Hartree/Molecule |
| Imaginary Frequency | -1709.14 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| N | 7.0 | 0.4760187500 | -1.3583822071 | -0.3054260226 |
| S | 16.0 | -0.9049451618 | -0.1656540501 | -0.5470034371 |
| O | 8.0 | -1.7270655491 | -0.2382651437 | 0.7300103482 |
| C | 6.0 | 0.7386853980 | 1.3954815210 | 0.2754232624 |
| C | 6.0 | 1.8506040837 | 0.6702395214 | 0.6888002533 |
| H | 1.0 | -0.0550431582 | 1.6263912710 | 0.9759896571 |
| H | 1.0 | 0.8004456127 | 2.0377888935 | -0.5944519532 |
| H | 1.0 | 1.3151496523 | -0.6822011151 | 0.1699006330 |
| H | 1.0 | 1.9341041542 | 0.3936009390 | 1.7323000989 |
| H | 1.0 | 2.7834401834 | 0.7742041263 | 0.1491651303 |
| H | 1.0 | 0.7708940309 | -1.8062412170 | -1.1713062529 |
| H | 1.0 | 0.1521677040 | -2.0624218390 | 0.3584228825 |

| | |
|---|---|
| Energy | -607.2699227 Hartree |
| ZPE | 0.094115 Hartree/Molecule |
| Imaginary Frequency | -956.90 $cm^{-1}$ |

MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -607.6167030 Hartree

**Zwitterion product-Ammonium Sulfenate**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .5211810682 | -.0001515974 | -.5530022009 |
| N | 7.0 | -.1915783422 | -.0000489168 | 1.6866684583 |
| H | 1.0 | -.7566162603 | -.8139993171 | 1.8315751159 |
| H | 1.0 | -.7567261702 | .8139064348 | 1.8313426209 |
| H | 1.0 | .5559709282 | .0001002530 | 2.3535339045 |
| O | 8.0 | -.7218364237 | .0001931435 | -1.341442287 |

Energy -528.4722405 Hartree
ZPE 0.042992 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .5449097802 | -.0001639503 | -.5643130978 |
| N | 7.0 | -.1821980555 | -.0000291340 | 1.6988089299 |
| H | 1.0 | -.7575496345 | -.8223297726 | 1.8379990903 |
| H | 1.0 | -.7576376833 | .8222020780 | 1.8377438702 |
| H | 1.0 | .5563788989 | .0001101308 | 2.3927731078 |
| O | 8.0 | -.7535085059 | .0002106481 | -1.3943363003 |

Energy -528.9747022 Hartree
ZPE 0.040676 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -529.2243794 Hartree

**(Z)-2-Butene Sulfinylmethane**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .0689920628 | -1.0324075191 | 1.0504265268 |
| C | 6.0 | -.3992134953 | -.4514589521 | 2.6838115462 |
| H | 1.0 | -.1375662356 | -1.2298024947 | 3.3884880097 |
| H | 1.0 | -1.4685455573 | -.2840206975 | 2.7194883151 |
| H | 1.0 | .1409538231 | .4556335340 | 2.9285139359 |
| O | 8.0 | -.8189521279 | -2.1849886089 | .7440172134 |
| C | 6.0 | -.5700562105 | .3728226327 | .1007554445 |
| C | 6.0 | -.4366525641 | .1067222772 | -1.3714730704 |
| H | 1.0 | -.0355391055 | 1.2572246773 | .4228211145 |
| H | 1.0 | -1.6174712125 | .4747300695 | .3687546210 |
| C | 6.0 | .2972572779 | .7762630723 | -2.2436339268 |
| H | 1.0 | -1.0110050315 | -.7338508744 | -1.7204556402 |
| C | 6.0 | 1.1858410770 | 1.9654046238 | -2.0109701077 |
| H | 1.0 | .2622432894 | .4371841739 | -3.2671889578 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .8682148077 | 2.8002760968 | -2.6299357219 |
| H | 1.0 | 2.2080605359 | 1.7308619595 | -2.2954526793 |
| H | 1.0 | 1.1963114663 | 2.2992981297 | -.9815224232 |

Energy -667.4682281 Hartree
ZPE 0.151512 Hartree/Molecule

MP2/6-31g(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .0935189652 | -1.0449217737 | 1.0364879889 |
| C | 6.0 | -.4059043960 | -.4453467714 | 2.6688361922 |
| H | 1.0 | -.1186291209 | -1.2013287428 | 3.3955317623 |
| H | 1.0 | -1.4871380174 | -.3190715153 | 2.6860485047 |
| H | 1.0 | .0984722448 | .4931881199 | 2.8938559405 |
| O | 8.0 | -.7974215579 | -2.2203588943 | .7020323450 |
| C | 6.0 | -.5571665112 | .3903295293 | .1094113285 |
| C | 6.0 | -.4546937507 | .1095436524 | -1.3531785921 |
| H | 1.0 | .0048981283 | 1.2710279926 | .4202978768 |
| H | 1.0 | -1.6021877833 | .5031683066 | .4097928395 |
| C | 6.0 | .2941289421 | .7753375421 | -2.2475235983 |
| H | 1.0 | -1.0422777879 | -.7353561501 | -1.6913572113 |
| C | 6.0 | 1.1839201309 | 1.9552931552 | -2.0039270983 |
| H | 1.0 | .2541011546 | .4291576367 | -3.2750172150 |
| H | 1.0 | .8741543591 | 2.8010075587 | -2.6193679637 |
| H | 1.0 | 2.2127008368 | 1.7195115596 | -2.2796495307 |
| H | 1.0 | 1.1823969631 | 2.2787108944 | -.9658293693 |

Energy -668.4898934 Hartree
ZPE 0.145205 Hartree/Molecule
CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p) -668.5955549 Hartree
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -668.8844665 Hartree

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16 | 0.148253 | -0.916256 | 0.985143 |
| C | 6 | -0.335587 | -0.267991 | 2.635266 |
| H | 1 | -0.085452 | -1.040356 | 3.365029 |
| H | 1 | -1.412435 | -0.081649 | 2.652728 |
| H | 1 | 0.223686 | 0.645346 | 2.856057 |
| O | 8 | -0.769196 | -2.078896 | 0.676217 |
| C | 6 | -0.482239 | 0.550966 | 0.015616 |
| C | 6 | -0.362207 | 0.283971 | -1.450321 |
| H | 1 | 0.086743 | 1.423146 | 0.349021 |
| H | 1 | -1.532021 | 0.666646 | 0.311870 |
| C | 6 | 0.374672 | 0.965095 | -2.337214 |
| H | 1 | -0.939331 | -0.569372 | -1.799203 |
| C | 6 | 1.246270 | 2.163117 | -2.095087 |

| | | | | |
|---|---|---|---|---|
| H | 1 | 0.341007 | 0.623993 | -3.371547 |
| H | 1 | 0.917878 | 3.012724 | -2.706977 |
| H | 1 | 2.282589 | 1.952046 | -2.386821 |
| H | 1 | 1.253390 | 2.487783 | -1.051739 |

Energy -669.9110822 Hartree
ZPE 0.141320 Hartree/Molecule

**Transition State for (*Z*)-2-Butene Sulfinylmethane**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.7009021366 | 0.5323112312 | 0.9156836491 |
| C | 6.0 | -0.0891941443 | -0.2466593640 | 2.3203582648 |
| H | 1.0 | 0.6747217862 | -0.7192136440 | 2.9222631738 |
| H | 1.0 | -0.8096147179 | -0.9810819427 | 1.9872705706 |
| H | 1.0 | -0.5799448726 | 0.5279087630 | 2.8976188736 |
| O | 8.0 | 1.3683490050 | -0.6626398079 | 0.1366587172 |
| C | 6.0 | -0.7964811339 | 1.1260101032 | -0.1434091329 |
| C | 6.0 | -0.5655317491 | 0.8748745159 | -1.5660838986 |
| H | 1.0 | -0.8566301051 | 2.1724197756 | 0.1247655818 |
| H | 1.0 | -1.6275448699 | 0.5840648414 | 0.2940557494 |
| C | 6.0 | -0.5956186907 | -0.4132634254 | -2.0352390059 |
| H | 1.0 | -0.2432408889 | 1.6909796616 | -2.1829586092 |
| C | 6.0 | -0.7850689813 | -1.5948050176 | -1.2963408774 |
| H | 1.0 | -0.3267027444 | -0.5376213982 | -3.0749505855 |
| H | 1.0 | -0.8966593560 | -2.5142349247 | -1.8463121407 |
| H | 1.0 | -1.4029044973 | -1.5494326122 | -0.4059703522 |
| H | 1.0 | 0.6881390236 | -1.1872685552 | -0.433304278 |

Energy -667.3715103 Hartree
ZPE 0.146963 Hartree/Molecule
Imaginary Frequency -536.29 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.7368937326 | 0.5834578394 | 0.9634474958 |
| C | 6.0 | -0.1535618497 | -0.3576141571 | 2.2035634724 |
| H | 1.0 | 0.5285799930 | -1.0931267906 | 2.6231170441 |
| H | 1.0 | -1.0314691181 | -0.8519577566 | 1.7927983712 |
| H | 1.0 | -0.4542082462 | 0.3428127280 | 2.9817910074 |
| O | 8.0 | 1.4566193869 | -0.4791409765 | -0.0019319530 |
| C | 6.0 | -0.8418540403 | 1.2271169239 | -0.2034080867 |
| C | 6.0 | -0.6032448596 | 0.8853978463 | -1.5655584705 |
| H | 1.0 | -0.8789309976 | 2.2876346998 | 0.0327841269 |
| H | 1.0 | -1.6391390977 | 0.6767133266 | 0.2999254786 |
| C | 6.0 | -0.5902273641 | -0.4516749732 | -1.9491874891 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.2324064700 | 1.6434172440 | -2.2392664394 |
| C | 6.0 | -0.7117134230 | -1.5666067720 | -1.0989778357 |
| H | 1.0 | -0.3051232386 | -0.6549665845 | -2.9788275738 |
| H | 1.0 | -0.7975526062 | -2.5405113613 | -1.5611170205 |
| H | 1.0 | -1.2981022365 | -1.4570885210 | -0.1898674077 |
| H | 1.0 | 0.6724156351 | -1.0915145152 | -0.4951790201 |

Energy -668.4077690 Hartree
ZPE 0.139669 Hartree/Molecule
Imaginary Frequency -1290.82 $cm^{-1}$
CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p) -668.5112053 Hartree
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -668.8035026 Hartree

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16 | 0.800709 | 0.536522 | 1.002357 |
| C | 6 | -0.175953 | -0.357299 | 2.250470 |
| H | 1 | 0.460895 | -1.121669 | 2.700621 |
| H | 1 | -1.071116 | -0.819001 | 1.824877 |
| H | 1 | -0.461973 | 0.372245 | 3.013931 |
| O | 8 | 1.422313 | -0.556288 | 0.007347 |
| C | 6 | -0.900651 | 1.265816 | -0.250654 |
| C | 6 | -0.640976 | 0.890419 | -1.592115 |
| H | 1 | -0.899722 | 2.326070 | -0.007022 |
| H | 1 | -1.653380 | 0.702956 | 0.302334 |
| C | 6 | -0.616349 | -0.446863 | -1.981735 |
| H | 1 | -0.272368 | 1.643294 | -2.281052 |
| C | 6 | -0.728760 | -1.578701 | -1.136049 |
| H | 1 | -0.313306 | -0.638039 | -3.012261 |
| H | 1 | -0.782649 | -2.554044 | -1.612862 |
| H | 1 | -1.367211 | -1.494498 | -0.252952 |
| H | 1 | 0.547109 | -1.191587 | -0.511604 |

Energy -669.8398238 Hartree
ZPE 0.135552 Hartree/Molecule
Imaginary Frequency -1792.96 $cm^{-1}$

***s-cis*-1,3-Butadiene**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.5941248684 | 0.0617068484 | -0.4303191094 |
| C | 6.0 | -1.5387478763 | -0.1350248522 | -0.4959144322 |
| C | 6.0 | -0.7306192908 | 0.1087587995 | 0.5205519743 |
| H | 1.0 | -1.1767151364 | -0.5486985039 | -1.4210376488 |
| H | 1.0 | -1.1496297387 | 0.4801423324 | 1.4431270138 |
| C | 6.0 | 0.7306385546 | -0.1086882331 | 0.5205901965 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.5387052097 | 0.1351497720 | -0.4958794476 |
| H | 1.0 | 1.1496785275 | -0.4801418102 | 1.4430935656 |
| H | 1.0 | 1.1767508999 | 0.5487298685 | -1.4210411488 |
| H | 1.0 | 2.5940637188 | -0.0619342215 | -0.4303127632 |

Energy -154.9255291 Hartree
ZPE 0.091089 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.5826149195 | 0.0725250950 | -0.4694644897 |
| C | 6.0 | -1.5222888379 | -0.1313104173 | -0.5057812966 |
| C | 6.0 | -0.7256721434 | 0.1124894346 | 0.5464859352 |
| H | 1.0 | -1.1272494502 | -0.5522108039 | -1.4204281786 |
| H | 1.0 | -1.1667062861 | 0.4839780367 | 1.4656045084 |
| C | 6.0 | 0.7256789568 | -0.1125242685 | 0.5465178480 |
| C | 6.0 | 1.5223075392 | 0.1313033190 | -0.5057747470 |
| H | 1.0 | 1.1667104881 | -0.4839677417 | 1.4655973656 |
| H | 1.0 | 1.1272236842 | 0.5521930689 | -1.4204397996 |
| H | 1.0 | 2.5826109688 | -0.0724757229 | -0.4694589455 |

Energy -155.4667681 Hartree
ZPE 0.086886 Hartree/Molecule
CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p) -155.5331833 Hartree
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -155.6221432 Hartree

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1 | -2.611797 | 0.054129 | -0.416899 |
| C | 6 | -1.541722 | -0.110824 | -0.492989 |
| C | 6 | -0.729984 | 0.084330 | 0.553459 |
| H | 1 | -1.165469 | -0.453080 | -1.453114 |
| H | 1 | -1.171372 | 0.373803 | 1.507169 |
| C | 6 | 0.729983 | -0.084330 | 0.553461 |
| C | 6 | 1.541723 | 0.110823 | -0.492985 |
| H | 1 | 1.171369 | -0.373805 | 1.507171 |
| H | 1 | 1.165472 | 0.453084 | -1.453111 |
| H | 1 | 2.611798 | -0.054127 | -0.416894 |

Energy -155.9960201 Hartree
ZPE 0.0851130 Hartree/Molecule

**Methyl Vinyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.5483635 | 0.4265580 | 0.1538664 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.2440177 | -0.2362087 | 1.7968127 |
| H | 1.0 | 1.2010827 | -0.3175290 | 2.2953918 |
| H | 1.0 | -0.2078754 | -1.2153610 | 1.7077628 |
| H | 1.0 | -0.3992058 | 0.4360055 | 2.3522355 |
| O | 8.0 | 1.2648884 | -0.6275605 | -0.6081123 |
| C | 6.0 | -1.1368038 | 0.4342133 | -0.4113799 |
| C | 6.0 | -1.5044457 | -0.2996049 | -1.4385275 |
| H | 1.0 | -1.7933612 | 1.1146080 | 0.1042688 |
| H | 1.0 | -0.7973794 | -0.9451472 | -1.9272509 |
| H | 1.0 | -2.5127939 | -0.2674193 | -1.8108041 |

Energy -589.3894731 Hartree
ZPE 0.091241 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.5724575529 | 0.4273174066 | 0.1366900428 |
| C | 6.0 | 0.2351598105 | -0.2316212735 | 1.7881449270 |
| H | 1.0 | 1.1865055214 | -0.3183938805 | 2.3079367372 |
| H | 1.0 | -0.2249022216 | -1.2121801782 | 1.6861290728 |
| H | 1.0 | -0.4204766937 | 0.4484280267 | 2.3295246756 |
| O | 8.0 | 1.2708677056 | -0.6554029215 | -0.6545877357 |
| C | 6.0 | -1.1385941206 | 0.4459132744 | -0.3841901480 |
| C | 6.0 | -1.5003188092 | -0.3008275565 | -1.4286837331 |
| H | 1.0 | -1.7971113311 | 1.1228341407 | 0.1465128820 |
| H | 1.0 | -0.7634472878 | -0.9298885719 | -1.9105443753 |
| H | 1.0 | -2.5136530262 | -0.2936242663 | -1.8026690454 |

Energy -590.1226350 Hartree
ZPE 0.087177 Hartree/Molecule
CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p) -590.1952732 Hartree
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -590.4376985 Hartree
Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16 | 0.564688 | 0.430950 | 0.146539 |
| C | 6 | 0.230176 | -0.236153 | 1.827967 |
| H | 1 | 1.192326 | -0.315402 | 2.337764 |
| H | 1 | -0.229562 | -1.221761 | 1.731587 |
| H | 1 | -0.424121 | 0.450486 | 2.371786 |
| O | 8 | 1.284248 | -0.641289 | -0.640310 |
| C | 6 | -1.162875 | 0.437716 | -0.394596 |
| C | 6 | -1.519390 | -0.298373 | -1.441187 |
| H | 1 | -1.817771 | 1.123338 | 0.138293 |
| H | 1 | -0.784565 | -0.937088 | -1.924935 |
| H | 1 | -2.532764 | -0.283600 | -1.829742 |

Energy -591.2729339 Hartree

ZPE 0.084891 Hartree/Molecule

**Transition State for Methyl Vinyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.2035423 | -0.5389722 | -1.7417287 |
| S | 16.0 | -0.5521522 | -0.6356048 | 0.0147323 |
| O | 8.0 | 0.8738968 | -0.9697960 | 0.6187467 |
| C | 6.0 | -0.3830285 | 1.4654180 | 0.5197222 |
| H | 1.0 | -1.1061374 | -0.2067396 | -2.2421581 |
| H | 1.0 | 0.5940722 | 0.1714945 | -1.9086173 |
| H | 1.0 | 0.0765621 | -1.5154317 | -2.1129814 |
| C | 6.0 | 0.7789650 | 1.6049011 | 0.9876428 |
| H | 1.0 | -1.3457646 | 1.8377340 | 0.2569280 |
| H | 1.0 | 1.2310341 | -0.0561696 | 0.8909813 |
| H | 1.0 | 1.2391294 | 2.5090746 | 1.3363387 |

Energy -589.3045198 Hartree
ZPE 0.086148 Hartree/Molecule
Imaginary Frequency -482.93 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.2141365648 | -0.5534080736 | -1.7302742174 |
| S | 16.0 | -0.5468962674 | -0.7792917322 | 0.0249222191 |
| O | 8.0 | 0.9105780034 | -0.8979785531 | 0.6478279333 |
| C | 6.0 | -0.4304408358 | 1.4846804421 | 0.4810499431 |
| H | 1.0 | -1.1500194389 | -0.2874216257 | -2.2214712684 |
| H | 1.0 | 0.5065002520 | 0.2509523614 | -1.8544983297 |
| H | 1.0 | 0.1730079478 | -1.4738405169 | -2.1588340598 |
| C | 6.0 | 0.7252972961 | 1.5762998436 | 0.9679810116 |
| H | 1.0 | -1.3729281793 | 1.8902829138 | 0.1742731788 |
| H | 1.0 | 1.1260815891 | 0.2052245282 | 0.9199425348 |
| H | 1.0 | 1.4620781980 | 2.2443845124 | 1.3678952546 |

Energy -590.0553647 Hartree
ZPE 0.080248 Hartree/Molecule
Imaginary Frequency -979.07 $cm^{-1}$
CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p) -590.1257127 Hartree
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -590.3660116 Hartree

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6 | -0.218542 | -0.550619 | -1.780094 |
| S | 16 | -0.560938 | -0.722157 | 0.003700 |
| O | 8 | 0.891934 | -0.895980 | 0.646529 |

| | | | | |
|---|---|---|---|---|
| C | 6 | -0.380526 | 1.580707 | 0.525005 |
| H | 1 | -1.171925 | -0.361909 | -2.283406 |
| H | 1 | 0.462624 | 0.285922 | -1.945324 |
| H | 1 | 0.216920 | -1.477245 | -2.158449 |
| C | 6 | 0.772851 | 1.608381 | 1.019002 |
| H | 1 | -1.331182 | 1.961756 | 0.208719 |
| H | 1 | 1.141031 | 0.173284 | 0.931031 |
| H | 1 | 1.479373 | 2.309728 | 1.432517 |

Energy -591.2110646 Hartree
ZPE 0.077910 Hartree/Molecule
Imaginary Frequency -720.12 $cm^{-1}$

**Acetylene**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.000000 | 0.000000 | 1.693090 |
| C | 6.0 | 0.000000 | 0.000000 | 0.597090 |
| C | 6.0 | 0.000000 | 0.000000 | -0.597090 |
| H | 1.0 | 0.000000 | 0.000000 | -1.693090 |

Energy -76.8178265 Hartree
ZPE 0.029163 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.0000000000 | 0.0000000000 | -1.6717553320 |
| C | 6.0 | 0.0000000000 | 0.0000000000 | -0.6092739913 |
| C | 6.0 | 0.0000000000 | 0.0000000000 | 0.6092739914 |
| H | 1.0 | 0.0000000000 | 0.0000000000 | 1.6717553319 |

Energy -77.0816680 Hartree
ZPE 0.026137 Hartree/Molecule
CCSD(T)/6-31G(d,p)//MP2/6-31G(d,p) -77.1091170 Hartree
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -77.1601092 Hartree

Becke3LYP/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1 | 0.000000 | 0.000000 | -1.668348 |
| C | 6 | 0.000000 | 0.000000 | -0.602660 |
| C | 6 | 0.000000 | 0.000000 | 0.602660 |
| H | 1 | 0.000000 | 0.000000 | 1.668348 |

Energy -77.3295725 Hartree
ZPE 0.026735 Hartree/Molecule

**1-Propene Sulfinylmethane**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .7941600148 | .3108653338 | .4411825964 |
| C | 6.0 | .5232364626 | .3720849744 | 2.2157040013 |
| H | 1.0 | 1.4964949807 | .3465144442 | 2.6874869538 |
| H | 1.0 | -.0469292166 | -.4928864988 | 2.5314958126 |
| H | 1.0 | .0129666281 | 1.2889669376 | 2.4856497644 |
| O | 8.0 | 1.4047525005 | -1.0118567784 | .1548882889 |
| C | 6.0 | -.9464427006 | .2031384241 | -.0578710074 |
| C | 6.0 | -1.0814316760 | .2544797041 | -1.5519390143 |
| H | 1.0 | -1.4706102938 | 1.0310539449 | .4099284353 |
| H | 1.0 | -1.3246627232 | -.7315823757 | .3402837784 |
| C | 6.0 | -1.2911812487 | -.8035292359 | -2.3081305683 |
| H | 1.0 | -.9741263917 | 1.2259102403 | -2.0071514928 |
| H | 1.0 | -1.3866073691 | -1.7900213667 | -1.8892822845 |
| H | 1.0 | -1.3669230349 | -.7197382217 | -3.3775327698 |

Energy -628.4269180 Hartree
ZPE 0.121282 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .7776868471 | .2654091867 | .3820540157 |
| C | 6.0 | .5260977290 | .3118743360 | 2.1734185466 |
| H | 1.0 | 1.5041428072 | .2248237488 | 2.6400958351 |
| H | 1.0 | -.0930631002 | -.5319062983 | 2.4734283220 |
| H | 1.0 | .0629303704 | 1.2544899714 | 2.4606578829 |
| O | 8.0 | 1.2641860094 | -1.1221066377 | .0340245590 |
| C | 6.0 | -1.0060424254 | .3171029599 | -.0421999165 |
| C | 6.0 | -1.1674492992 | .3040976269 | -1.5266006458 |
| H | 1.0 | -1.4387903290 | 1.2072233676 | .4171566359 |
| H | 1.0 | -1.4409050457 | -.5759038275 | .4112789990 |
| C | 6.0 | -1.1452650824 | -.8283185535 | -2.2407093489 |
| H | 1.0 | -1.2395532403 | 1.2611946626 | -2.0294955516 |
| H | 1.0 | -1.0433690609 | -1.7909875061 | -1.7597585166 |
| H | 1.0 | -1.2179102479 | -.8135935107 | -3.3186383227 |

Energy -629.3044626 Hartree
ZPE 0.116062 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -629.6600823 Hartree

**Transition State for 1-Propene Sulfinylmethane**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -1.0680104613 | -.2104754200 | .8098593579 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.9232738964 | 1.4994270914 | 1.3397246211 |
| H | 1.0 | -1.8721141242 | 2.0003315758 | 1.2033632058 |
| H | 1.0 | -.1624895149 | 2.0045670611 | .7580307722 |
| H | 1.0 | -.6568756886 | 1.5095236529 | 2.3908543622 |
| O | 8.0 | -1.2892884967 | -.0855431233 | -.7263457020 |
| C | 6.0 | 1.2010634398 | -.6275496548 | .4431389596 |
| C | 6.0 | 1.2021172792 | -.3903550385 | -.9253383351 |
| H | 1.0 | 1.1909112929 | -1.6349659579 | .8221022009 |
| H | 1.0 | 1.5585483137 | .1112932930 | 1.1407622248 |
| C | 6.0 | 2.0676582736 | -.3386832021 | -1.9145438537 |
| H | 1.0 | -.1984167782 | -.1816855301 | -1.122684505 |
| H | 1.0 | 3.1235615006 | -.5257126972 | -1.7832966064 |
| H | 1.0 | 1.7547061605 | -.1107917504 | -2.9197791568 |

Energy -628.3330794 Hartree
ZPE 0.114496 Hartree/Molecule
Imaginary Frequency -1681.44 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -1.1588817772 | -.2235514913 | .7924495491 |
| C | 6.0 | -.8994542680 | 1.4876214108 | 1.2855783961 |
| H | 1.0 | -1.7875318640 | 2.0757606122 | 1.0707935686 |
| H | 1.0 | -.0502240821 | 1.8956437105 | .7408211029 |
| H | 1.0 | -.6959700436 | 1.5083074715 | 2.3559907571 |
| O | 8.0 | -1.2441742042 | -.1102942204 | -.7907289286 |
| C | 6.0 | 1.2277224110 | -.6603171130 | .5242543389 |
| C | 6.0 | 1.2400309739 | -.4086406589 | -.8297072454 |
| H | 1.0 | 1.2023080816 | -1.6781916118 | .8963338433 |
| H | 1.0 | 1.5501729994 | .0878291669 | 1.2404255486 |
| C | 6.0 | 1.9977222097 | -.2737009034 | -1.9160974506 |
| H | 1.0 | -.0993580713 | -.2364471433 | -1.0942375640 |
| H | 1.0 | 3.0711249243 | -.4237400044 | -1.8808112673 |
| H | 1.0 | 1.5746100102 | -.0208989255 | -2.8792170489 |

Energy -629.2371772 Hartree
ZPE 0.109260 Hartree/Molecule
Imaginary Frequency -1021.51 $cm^{-1}$
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -629.5852535 Hartree

**Allene**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.8503761039 | -.0000000947 | .9216291309 |
| C | 6.0 | -1.2956465260 | .0000000959 | -.0002113206 |
| C | 6.0 | -.0000034205 | .0000007357 | .0001028619 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.8498941906 | -.0000001230 | -.9223174094 |
| C | 6.0 | 1.2956494938 | -.0000016909 | .0003365256 |
| H | 1.0 | 1.8501338036 | -.9219711618 | .0004181910 |
| H | 1.0 | 1.8501339436 | .9219722388 | .0004182206 |

Energy -115.8685572 Hartree
ZPE 0.059161 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.8720744984 | -.0000063556 | .9249352675 |
| C | 6.0 | -1.3124228693 | .0000104752 | -.0002397694 |
| C | 6.0 | -.0000075203 | .0000053159 | .0000881117 |
| H | 1.0 | -1.8716062379 | -.0000063691 | -.9256062381 |
| C | 6.0 | 1.3124179309 | .0000023315 | .0003297283 |
| H | 1.0 | 1.8718434492 | -.9252838397 | .0004345418 |
| H | 1.0 | 1.8718467458 | .9252784418 | .0004345582 |

Energy -116.2657090 Hartree
ZPE 0.056499 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -116.3826177 Hartree

**3-Methanesulfinyl-1-propanal**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .6989683727 | -.0050774929 | .8682944546 |
| C | 6.0 | .3115540897 | -.0262746288 | 2.6198778402 |
| H | 1.0 | 1.2511750184 | -.0559839383 | 3.1552994963 |
| H | 1.0 | -.2613857892 | -.9142779747 | 2.8562392477 |
| H | 1.0 | -.2332546075 | .8697000159 | 2.8924926041 |
| O | 8.0 | 1.2997856763 | -1.3238010759 | .5418890028 |
| C | 6.0 | -.9965719283 | -.0589910088 | .2435797933 |
| C | 6.0 | -1.0145268914 | -.1186304263 | -1.2840393095 |
| H | 1.0 | -1.5238963212 | .8149782152 | .6157206674 |
| H | 1.0 | -1.4605310912 | -.9475840517 | .6554589668 |
| H | 1.0 | -.3662888236 | -.9049241367 | -1.6491807544 |
| C | 6.0 | -.6384726678 | 1.1854245955 | -1.9499222234 |
| H | 1.0 | -2.0288264483 | -.3514717209 | -1.6036926135 |
| O | 8.0 | -.0136888809 | 1.2603838320 | -2.9547972033 |
| H | 1.0 | -1.0122167079 | 2.0941019965 | -1.4581142692 |

Energy -703.3035264 Hartree
ZPE 0.126303 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.7014116888 | 0.0477664740 | 0.8336300256 |
| C | 6.0 | 0.3079952526 | -0.0370351207 | 2.5954413324 |
| H | 1.0 | 1.2479276275 | -0.0190460602 | 3.1412838849 |
| H | 1.0 | -0.2130771112 | -0.9707139801 | 2.8003768657 |
| H | 1.0 | -0.3006498922 | 0.8195452833 | 2.8809570785 |
| O | 8.0 | 1.3462380779 | -1.2614295515 | 0.4391311322 |
| C | 6.0 | -1.0265967019 | -0.0350975919 | 0.2621137422 |
| C | 6.0 | -1.0455004743 | -0.1286587233 | -1.2583901063 |
| H | 1.0 | -1.5502987195 | 0.8543204039 | 0.6218139869 |
| H | 1.0 | -1.4786400955 | -0.9224801049 | 0.7081201867 |
| H | 1.0 | -0.4070776470 | -0.9421615727 | -1.6011930889 |
| C | 6.0 | -0.6067696021 | 1.1557542154 | -1.9212248988 |
| H | 1.0 | -2.0682656885 | -0.3354017776 | -1.5873022581 |
| O | 8.0 | 0.1160565233 | 1.2123126495 | -2.9039471704 |
| H | 1.0 | -1.0109302382 | 2.0798976569 | -1.4617050128 |

Energy -704.3585969 Hartree
ZPE 0.120709 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -704.8042226 Hartree

**Transition State for 3-Methanesulfinyl-1-propanal**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -1.3493330651 | 0.2116048179 | 0.8056544454 |
| C | 6.0 | -1.1080345863 | 1.8371941636 | 1.5205989259 |
| H | 1.0 | -1.0063160864 | 1.7251939509 | 2.5938700507 |
| H | 1.0 | -1.9746635357 | 2.4445540239 | 1.2994146223 |
| H | 1.0 | -0.2220997906 | 2.2957142229 | 1.1017817342 |
| O | 8.0 | -1.3108023950 | 0.4769967751 | -0.7244122281 |
| C | 6.0 | 0.5499862846 | -0.4838795690 | 0.8946841967 |
| H | 1.0 | -0.2155196621 | 0.2929290549 | -0.9481176498 |
| H | 1.0 | 0.3901874553 | -1.5353329830 | 1.0839900300 |
| H | 1.0 | 0.9309785476 | 0.0110689669 | 1.7749683147 |
| C | 6.0 | 1.1246588014 | -0.1410290741 | -0.3921914850 |
| C | 6.0 | 1.5269507439 | -1.2293686382 | -1.2710104341 |
| H | 1.0 | 1.7657323803 | 0.7259996220 | -0.4254914774 |
| O | 8.0 | 2.3113045767 | -1.1536260890 | -2.1711825885 |
| H | 1.0 | 1.0155744315 | -2.1869740448 | -1.0735653570 |

Energy -703.2463697 Hartree
ZPE 0.121054 Hartree/Molecule
Imaginary Frequency -1300.91 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -1.4342495971 | 0.2075331935 | 0.7805108066 |
| C | 6.0 | -1.1340999234 | 1.8186784649 | 1.5208611554 |
| H | 1.0 | -1.1113652024 | 1.6966030420 | 2.6034608978 |
| H | 1.0 | -1.9365616319 | 2.4966784551 | 1.2442385408 |
| H | 1.0 | -0.1821562288 | 2.2108350438 | 1.1691203599 |
| O | 8.0 | -1.2689124476 | 0.4862303928 | -0.7711970650 |
| C | 6.0 | 0.6302326366 | -0.4824955713 | 0.9168966520 |
| H | 1.0 | -0.1302502356 | 0.2717461419 | -0.9169634273 |
| H | 1.0 | 0.4631992220 | -1.5367042667 | 1.1203070673 |
| H | 1.0 | 0.9545330337 | 0.0715011955 | 1.7912140660 |
| C | 6.0 | 1.1430834073 | -0.1391359343 | -0.3608296057 |
| C | 6.0 | 1.4803872069 | -1.2318764184 | -1.2805877299 |
| H | 1.0 | 1.7523910233 | 0.7530825389 | -0.4580850738 |
| O | 8.0 | 2.2488349477 | -1.1472519446 | -2.2323298893 |
| H | 1.0 | 0.9535378896 | -2.1843791331 | -1.0576256549 |

| | |
|---|---|
| Energy | -704.3232750 Hartree |
| ZPE | 0.115584 Hartree/Molecule |
| Imaginary Frequency | - 893.43 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -704.7640594 Hartree |

**Acrolein**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.3675538010 | .0000000000 | 1.3969042958 |
| C | 6.0 | .4367392878 | .0000000000 | .8201695435 |
| O | 8.0 | -.6160468743 | .0000000000 | 1.3767700936 |
| C | 6.0 | .6037021445 | .0000000000 | -.6562990854 |
| C | 6.0 | -.4390440416 | .0000000000 | -1.4670885920 |
| H | 1.0 | 1.6118088730 | .0000000000 | -1.0352786494 |
| H | 1.0 | -1.4383526643 | .0000000000 | -1.0706185496 |
| H | 1.0 | -.3252115091 | .0000000000 | -2.5361777625 |

| | |
|---|---|
| Energy | -190.7667912 Hartree |
| ZPE | 0.066172 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.3753822445 | .0000000000 | 1.4090853818 |
| C | 6.0 | .4450909778 | .0000000000 | .8158310317 |
| O | 8.0 | -.6477624887 | .0000000000 | 1.3744899607 |
| C | 6.0 | .6199009672 | .0000000000 | -.6559677790 |
| C | 6.0 | -.4433764112 | .0000000000 | -1.4724416784 |
| H | 1.0 | 1.6317425976 | .0000000000 | -1.0417393701 |
| H | 1.0 | -1.4402822226 | .0000000000 | -1.0535102511 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -.3395466478 | .0000000000 | -2.5473660018 |

Energy -191.3409002 Hartree
ZPE 0.062645 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -191.5457595 Hartree

**2-Methanesulfinyl-1-propanal**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .9841804357 | .2478930171 | -.3191497985 |
| C | 6.0 | .4938095085 | 1.9715506824 | -.3925310050 |
| H | 1.0 | 1.2858460038 | 2.5058707056 | -.9004481836 |
| H | 1.0 | .3989784306 | 2.3467057626 | .6186841741 |
| H | 1.0 | -.4367562335 | 2.0743719849 | -.9325209557 |
| O | 8.0 | 2.0670493173 | .1582732964 | .6932456364 |
| C | 6.0 | -.5211301285 | -.4270795782 | .4874331090 |
| C | 6.0 | -.1722904590 | -1.7554669739 | 1.1538992127 |
| H | 1.0 | .6278599532 | -1.6150066773 | 1.8659781459 |
| H | 1.0 | -.8411533790 | .2997155636 | 1.2255864660 |
| H | 1.0 | .1488853078 | -2.4925810281 | .4237547373 |
| H | 1.0 | -1.0408026512 | -2.1481708698 | 1.6729274793 |
| C | 6.0 | -1.6184490837 | -.5705755525 | -.5493732573 |
| O | 8.0 | -2.2633243830 | .3415768066 | -.9537626677 |
| H | 1.0 | -1.7857012390 | -1.5839071393 | -.9289256928 |

Energy -703.3039907 Hartree
ZPE 0.126123 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 1.0082381509 | .2254837641 | -.3399726897 |
| C | 6.0 | .4751072923 | 1.9503942901 | -.3584628602 |
| H | 1.0 | 1.2111350831 | 2.5184624528 | -.9220867526 |
| H | 1.0 | .4504926654 | 2.3019309730 | .6718211621 |
| H | 1.0 | -.5072094135 | 2.0247749972 | -.8194017272 |
| O | 8.0 | 2.1181548985 | .0995507515 | .6771968340 |
| C | 6.0 | -.5390316552 | -.4231120603 | .4766997398 |
| C | 6.0 | -.1842202203 | -1.7273503942 | 1.1688300139 |
| H | 1.0 | .6699024453 | -1.5710454344 | 1.8237336109 |
| H | 1.0 | -.8552802104 | .3395689208 | 1.1909847881 |
| H | 1.0 | .0812191317 | -2.4956067909 | .4418242606 |
| H | 1.0 | -1.0267335905 | -2.0852176480 | 1.7586201915 |
| C | 6.0 | -1.5945064504 | -.5723654959 | -.5877747025 |
| O | 8.0 | -2.2523099537 | .3620857740 | -1.0316610785 |
| H | 1.0 | -1.7279567731 | -1.5943840997 | -.9855533899 |

| | |
|---|---|
| Energy | -704.3637577 Hartree |
| ZPE | 0.120845 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -704.8078289 Hartree |

**Transition State for 2-Methanesulfinyl-1-propanal**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.8010730565 | .0587120038 | -1.8932448269 |
| S | 16.0 | .9604089459 | -.8343804702 | -.5800697083 |
| O | 8.0 | 1.8611368918 | -.6294709254 | .6558659130 |
| C | 6.0 | -.3784888615 | .9172775589 | .1238912961 |
| C | 6.0 | .3284824361 | 1.2743017644 | 1.2918001668 |
| C | 6.0 | -1.6783404741 | .1920691674 | .2156243295 |
| H | 1.0 | -.2917744402 | 1.5095625150 | -.7705221183 |
| H | 1.0 | 1.3121050809 | .3389902176 | 1.1992273274 |
| H | 1.0 | -.1497712418 | 1.0492636058 | 2.2346882135 |
| H | 1.0 | .8478713859 | 2.2193639976 | 1.2747408337 |
| H | 1.0 | 2.7034745169 | -.4722580666 | -2.1647150874 |
| H | 1.0 | 2.0564453501 | 1.0566174381 | -1.5616393351 |
| H | 1.0 | 1.1365599900 | .1075984591 | -2.7481766337 |
| O | 8.0 | -2.4987765285 | .2202303528 | -.6435463231 |
| H | 1.0 | -1.8370908080 | -.3705933183 | 1.1407021528 |

| | |
|---|---|
| Energy | -703.2350493 Hartree |
| ZPE | 0.120134 Hartree/Molecule |
| Imaginary Frequency | -1805.77 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.7807712048 | .0557150912 | -1.8806107853 |
| S | 16.0 | .9871070552 | -.9126812180 | -.5841807886 |
| O | 8.0 | 1.8757680353 | -.6271917546 | .6912693814 |
| C | 6.0 | -.3976284608 | .9536847027 | .1148225159 |
| C | 6.0 | .3325635477 | 1.2660175054 | 1.2773896524 |
| C | 6.0 | -1.6685077893 | .2200884308 | .2019689600 |
| H | 1.0 | -.2756995504 | 1.5378632269 | -.7914562288 |
| H | 1.0 | 1.3079805981 | .3396117550 | 1.1958022532 |
| H | 1.0 | -.1253054478 | 1.0116475795 | 2.2285602261 |
| H | 1.0 | .8997653625 | 2.1892310694 | 1.2842274954 |
| H | 1.0 | 2.7202434711 | -.4098720319 | -2.1664530324 |
| H | 1.0 | 1.9663093551 | 1.0653908135 | -1.5221130759 |
| H | 1.0 | 1.1068510281 | .0854007986 | -2.7362540534 |
| O | 8.0 | -2.4939895716 | .1541597588 | -.7067200844 |
| H | 1.0 | -1.8429135380 | -.2917814274 | 1.1683737644 |

| | |
|---|---|
| Energy | -704.3216378 Hartree |
| ZPE | 0.114407 Hartree/Molecule |
| Imaginary Frequency | -1034.91 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -704.7611809 Hartree |

**3-Methanesulfinyl-2-butanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -2.2038297171 | 0.2672009060 | -1.3446044740 |
| S | 16.0 | -1.2260860947 | -0.0610458795 | 0.1250848076 |
| O | 8.0 | -1.1835112302 | -1.5406054573 | 0.2872939288 |
| C | 6.0 | 0.4176284743 | 0.4563823675 | -0.4990250000 |
| H | 1.0 | -3.2205458078 | -0.0148674731 | -1.1045796916 |
| H | 1.0 | -1.8574741253 | -0.3348214867 | -2.1730981454 |
| H | 1.0 | -2.1673835592 | 1.3223864172 | -1.5853237210 |
| C | 6.0 | 1.3286580975 | 0.6702360360 | 0.7132160328 |
| H | 1.0 | 0.2753127200 | 1.4403927017 | -0.9300096537 |
| C | 6.0 | 0.9888755148 | -0.5305561116 | -1.5180280127 |
| H | 1.0 | 0.9481352135 | -1.5433313313 | -1.1409053923 |
| H | 1.0 | 2.0194791702 | -0.2742355813 | -1.7417106407 |
| H | 1.0 | 0.4371668859 | -0.4927277718 | -2.4490195822 |
| O | 8.0 | 1.5938238709 | 1.7809768834 | 1.0536092671 |
| C | 6.0 | 1.8634398304 | -0.5437226622 | 1.4343363677 |
| H | 1.0 | 2.6542983016 | -0.9963003993 | 0.8428522615 |
| H | 1.0 | 1.0915370707 | -1.2917397425 | 1.5707385877 |
| H | 1.0 | 2.2724153846 | -0.2350242152 | 2.3861427604 |

| | |
|---|---|
| Energy | -742.3521637 Hartree |
| ZPE | 0.156186 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -2.1735732775 | .2647756122 | -1.3418476711 |
| S | 16.0 | -1.2198457463 | -.0656180860 | .1587339873 |
| O | 8.0 | -1.1508308300 | -1.5715040580 | .3219340905 |
| C | 6.0 | .4254343926 | .4796536481 | -.5061307409 |
| H | 1.0 | -3.1942138598 | -.0474325047 | -1.1332768441 |
| H | 1.0 | -1.7829693410 | -.3182980062 | -2.1720470141 |
| H | 1.0 | -2.1508050750 | 1.3302767374 | -1.5633943684 |
| C | 6.0 | 1.3192537397 | .6938236012 | .7092024730 |
| H | 1.0 | .2630228426 | 1.4647873609 | -.9480952405 |
| C | 6.0 | .9697812351 | -.5392188536 | -1.4969452625 |
| H | 1.0 | .8441600765 | -1.5450926386 | -1.0987422795 |
| H | 1.0 | 2.0268722332 | -.3558664253 | -1.6857052175 |
| H | 1.0 | .4482398762 | -.4798678390 | -2.4500615040 |

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 1.5527535106 | 1.8316610149 | 1.1069753773 |
| C | 6.0 | 1.8602192597 | -.5377289349 | 1.3908043473 |
| H | 1.0 | 2.6380909971 | -.9884620998 | .7731647144 |
| H | 1.0 | 1.0718247891 | -1.2808669504 | 1.5122434356 |
| H | 1.0 | 2.2845251774 | -.2564243782 | 2.3501574173 |

| | |
|---|---|
| Energy | -743.5573724 Hartree |
| ZPE | 0.149847 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -744.0407450637 Hartree |

**Transition State for 3-Methanesulfinyl-2-butanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.7681978653 | 0.0545935483 | -1.9271030030 |
| S | 16.0 | 0.9106128509 | -0.8375932586 | -0.6249674521 |
| O | 8.0 | 1.8411340092 | -0.7046672078 | 0.6011129161 |
| C | 6.0 | -0.3495178080 | 0.9406891071 | 0.1563623540 |
| C | 6.0 | 0.4215507410 | 1.2693418035 | 1.2926933911 |
| C | 6.0 | -1.6859369711 | 0.2545558398 | 0.2273809041 |
| H | 1.0 | -0.2689617367 | 1.5415313221 | -0.7323926701 |
| H | 1.0 | 1.3541945181 | 0.2873772058 | 1.1640884108 |
| H | 1.0 | -0.0127494119 | 1.0785350554 | 2.2616148208 |
| H | 1.0 | 0.9798459175 | 2.1908369122 | 1.2368243853 |
| H | 1.0 | 2.6573071254 | -0.4930829246 | -2.2089225456 |
| H | 1.0 | 2.0478116923 | 1.0415412948 | -1.5824786127 |
| H | 1.0 | 1.1024826697 | 0.1320607461 | -2.7788827589 |
| O | 8.0 | -2.4635917166 | 0.4037969929 | -0.6657785916 |
| C | 6.0 | -2.0083929385 | -0.5922090849 | 1.4354960909 |
| H | 1.0 | -2.2821470205 | 0.0536279043 | 2.2645531539 |
| H | 1.0 | -1.1598634308 | -1.1892359326 | 1.7496404480 |
| H | 1.0 | -2.8480011553 | -1.2310013238 | 1.2001002589 |

| | |
|---|---|
| Energy | -742.2834862 Hartree |
| ZPE | 0.150023 Hartree/Molecule |
| Imaginary Frequency | -1802.56 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.7471963134 | 0.0486555125 | -1.8942218778 |
| S | 16.0 | 0.8855436694 | -0.9114663370 | -0.6367525467 |
| O | 8.0 | 1.7927044059 | -0.7386244593 | 0.6478779278 |
| C | 6.0 | -0.3803743381 | 0.9871380546 | 0.1363981306 |
| C | 6.0 | 0.4076086164 | 1.2684351414 | 1.2688362558 |
| C | 6.0 | -1.6795117978 | 0.2787968512 | 0.2063416541 |
| H | 1.0 | -0.2746110837 | 1.5884633868 | -0.7610699186 |
| H | 1.0 | 1.3126430044 | 0.2678023512 | 1.1643559247 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.0113649508 | 1.0567491620 | 2.2456662227 |
| H | 1.0 | 1.0249181351 | 2.1585273181 | 1.2309851931 |
| H | 1.0 | 2.6655107820 | -0.4570810786 | -2.1807437546 |
| H | 1.0 | 1.9787429166 | 1.0370606641 | -1.5041369262 |
| H | 1.0 | 1.0881524870 | 0.1376296158 | -2.7572803189 |
| O | 8.0 | -2.4977622490 | 0.3753728149 | -0.7124085117 |
| C | 6.0 | -1.9576876115 | -0.5731623660 | 1.4254007116 |
| H | 1.0 | -2.2304901553 | 0.0639608622 | 2.2677206666 |
| H | 1.0 | -1.0796652848 | -1.1493223746 | 1.7173097819 |
| H | 1.0 | -2.7875776594 | -1.2382371193 | 1.2050628855 |

| | |
|---|---|
| Energy | -743.5145867 Hartree |
| ZPE | 0.143518 Hartree/Molecule |
| Imaginary Frequency | -1046.96 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -743.9940936 Hartree |

**Methyl Vinyl Ketone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .1540570120 | -.0000011969 | -.4336486616 |
| C | 6.0 | -.6696892548 | -.0000047902 | .8147702501 |
| C | 6.0 | -.1060484782 | .0000004386 | 2.0082721753 |
| H | 1.0 | -1.7413404310 | .0000011815 | .7060532028 |
| H | 1.0 | .9645654314 | .0000096139 | 2.1047069965 |
| H | 1.0 | -.6915754130 | -.0000063574 | 2.9101985535 |
| O | 8.0 | 1.3483221807 | -.0000013382 | -.4010053588 |
| C | 6.0 | -.6067837476 | .0000028027 | -1.7385401441 |
| H | 1.0 | -1.2482282167 | -.8751924919 | -1.7970194263 |
| H | 1.0 | -1.2482239619 | .8751978237 | -1.7970189715 |
| H | 1.0 | .0867490791 | -.0000056858 | -2.5673802158 |

| | |
|---|---|
| Energy | -229.8166007 Hartree |
| ZPE | 0.095865 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .1443834941 | -.0000020453 | -.4328787655 |
| C | 6.0 | -.6835358341 | .0000030921 | .8088368104 |
| C | 6.0 | -.1045134919 | -.0000016023 | 2.0168072580 |
| H | 1.0 | -1.7619224225 | .0000011066 | .7039104745 |
| H | 1.0 | .9742789646 | -.0000062824 | 2.0909661209 |
| H | 1.0 | -.6829513985 | .0000062440 | 2.9290704950 |
| O | 8.0 | 1.3738124406 | -.0000000696 | -.3897009083 |
| C | 6.0 | -.6086649643 | .0000017316 | -1.7421038114 |
| H | 1.0 | -1.2519542977 | -.8787010102 | -1.8031869038 |
| H | 1.0 | -1.2519663548 | .8786970607 | -1.8031801070 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .0948380647 | .0000017751 | -2.5691522628 |

Energy -230.5342904 Hartree
ZPE 0.091397 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -230.7785575 Hartree

**3-Ethenesulfinyl-2-butanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.8145465356 | -0.8766587281 | -1.6761512274 |
| S | 16.0 | 1.2710775523 | 0.1023547871 | -0.2614110155 |
| O | 8.0 | 1.8095021578 | 1.3887011319 | -0.7853008831 |
| C | 6.0 | -0.4012732518 | 0.5394129186 | 0.3298045568 |
| C | 6.0 | 1.0773714662 | -0.4449427392 | -2.8906290528 |
| H | 1.0 | 0.3966597969 | -1.8407548371 | -1.4525478095 |
| H | 1.0 | 1.5281554963 | 0.5185609892 | -3.0440241541 |
| H | 1.0 | 0.8538678476 | -1.0501798538 | -3.7510867808 |
| C | 6.0 | -0.2431663600 | 1.4911995195 | 1.5251083105 |
| C | 6.0 | -1.2167489393 | -0.6873777402 | 0.7007661780 |
| H | 1.0 | -0.8689645602 | 1.0701111809 | -0.4933630840 |
| H | 1.0 | 0.3816680009 | 2.3261321436 | 1.2376327074 |
| H | 1.0 | 0.2152374614 | 0.9819133498 | 2.3661831452 |
| H | 1.0 | -1.2061708242 | 1.8774726570 | 1.8390760045 |
| O | 8.0 | -0.6890621197 | -1.7265536521 | 0.9584677227 |
| C | 6.0 | -2.7187622117 | -0.5307152144 | 0.7150811828 |
| H | 1.0 | -3.1683084247 | -1.4055425166 | 1.1636282992 |
| H | 1.0 | -3.0241432169 | 0.3602673528 | 1.2518709169 |
| H | 1.0 | -3.0716615064 | -0.4304710488 | -0.3079189170 |

Energy -780.1970472 Hartree
ZPE 0.161829 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.7661222469 | -0.8840241044 | -1.6453398162 |
| S | 16.0 | 1.2978399024 | 0.0705221377 | -0.2252120159 |
| O | 8.0 | 1.8916932908 | 1.3617300652 | -0.7548455516 |
| C | 6.0 | -0.3988782986 | 0.5332923788 | 0.3228906232 |
| C | 6.0 | 1.0422862200 | -0.4160681681 | -2.8645008357 |
| H | 1.0 | 0.3100716946 | -1.8409154277 | -1.4315343046 |
| H | 1.0 | 1.5395474090 | 0.5395245885 | -2.9696357162 |
| H | 1.0 | 0.7808201374 | -0.9739306012 | -3.7519029079 |
| C | 6.0 | -0.2520808305 | 1.5081833934 | 1.4914902381 |
| C | 6.0 | -1.2002098333 | -0.6943565701 | 0.7001393188 |
| H | 1.0 | -0.8493486238 | 1.0452860039 | -0.5327160819 |
| H | 1.0 | 0.3925001767 | 2.3304065960 | 1.1865978710 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.1928030742 | 1.0080905937 | 2.3514486456 |
| H | 1.0 | -1.2199338548 | 1.9132823643 | 1.7825173016 |
| O | 8.0 | -0.6423068312 | -1.7527145773 | 0.9871450727 |
| C | 6.0 | -2.7016319358 | -0.5505259734 | 0.7042240896 |
| H | 1.0 | -3.1500337090 | -1.4382572447 | 1.1411995297 |
| H | 1.0 | -3.0090266829 | 0.3366302890 | 1.2563127723 |
| H | 1.0 | -3.0504086519 | -0.4332260437 | -0.3230921329 |

| | |
|---|---|
| Energy | -781.5209240 Hartree |
| ZPE | 0.154598 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -782.0392952 Hartree |

**Transition State for 3-Ethenesulfinyl-2-butanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.3157124175 | .0361216041 | 2.2270110804 |
| S | 16.0 | .9751915446 | -.8492063653 | -.5759205712 |
| O | 8.0 | 1.8582862416 | -.6784585148 | .6757311383 |
| C | 6.0 | -.3556645167 | .9513928954 | .1602248983 |
| C | 6.0 | .3920583786 | 1.2910591279 | 1.3066967323 |
| C | 6.0 | -1.6758788417 | .2337682843 | .2025902796 |
| H | 1.0 | -.2441630663 | 1.5316325374 | -.7373998073 |
| H | 1.0 | 1.3233675067 | .3359096737 | 1.2111514412 |
| H | 1.0 | -.0600214879 | 1.1041855440 | 2.2685706992 |
| H | 1.0 | .9441157264 | 2.2162560583 | 1.2526990501 |
| H | 1.0 | -1.1603986708 | -1.1904229934 | 1.7469504183 |
| H | 1.0 | -2.8339194212 | -1.2650634427 | 1.1587628857 |
| C | 6.0 | 1.8056546741 | .0447258581 | -1.8514836733 |
| O | 8.0 | -2.4326860947 | .3598184822 | -.7117101683 |
| C | 6.0 | -2.0113251904 | -.6101627618 | 1.4090702233 |
| C | 6.0 | 2.9765385699 | .6270439634 | -1.7005822963 |
| H | 1.0 | 1.2614738628 | .0547459421 | -2.7811771309 |
| H | 1.0 | 3.4350898207 | 1.1505527890 | -2.5199007554 |
| H | 1.0 | 3.5045599119 | .5853187702 | -.7661526688 |

| | |
|---|---|
| Energy | -780.1270610 Hartree |
| ZPE | 0.155843 Hartree/Molecule |
| Imaginary Frequency | -1796.39 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.2311616289 | 0.0796473323 | 2.2417200373 |
| S | 16.0 | 0.9225359020 | -0.9432215141 | -0.6209841423 |
| O | 8.0 | 1.7955336413 | -0.7611895322 | 0.6794304860 |
| C | 6.0 | -0.3732354240 | 0.9745162817 | 0.1022429771 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.4150830630 | 1.2767022483 | 1.2302488200 |
| C | 6.0 | -1.6632723738 | 0.2522040206 | 0.1805292183 |
| H | 1.0 | -0.2526876221 | 1.5485971753 | -0.8099913641 |
| H | 1.0 | 1.3018919159 | 0.2881017783 | 1.1672916544 |
| H | 1.0 | -0.0141967992 | 1.0965947054 | 2.2093874298 |
| H | 1.0 | 1.0299174699 | 2.1671276338 | 1.1697711145 |
| H | 1.0 | -1.0586058951 | -1.1307642158 | 1.7318026764 |
| H | 1.0 | -2.7599585524 | -1.2552717094 | 1.2058443683 |
| C | 6.0 | 1.7614074035 | 0.0261586039 | -1.8349421399 |
| O | 8.0 | -2.4757407083 | 0.3165547217 | -0.7468028445 |
| C | 6.0 | -1.9412973880 | -0.5736602356 | 1.4176362590 |
| C | 6.0 | 2.9087361283 | 0.6658663122 | -1.5855638932 |
| H | 1.0 | 1.2548391646 | 0.0536787772 | -2.7928026785 |
| H | 1.0 | 3.3863503667 | 1.2561121003 | -2.3532878997 |
| H | 1.0 | 3.3804278668 | 0.5914629682 | -0.6163983036 |

| | |
|---|---|
| Energy | -781.4792764 Hartree |
| ZPE | 0.148441 Hartree/Molecule |
| Imaginary Frequency | -1046.55 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -781.9953966 Hartree |

**Cyclopropyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.7480467480 | 2.0658002624 | -1.1630411567 |
| C | 6.0 | 0.8392532710 | 1.9411679738 | -0.0983517820 |
| C | 6.0 | -0.4174010876 | 1.8806366519 | 0.7047983298 |
| C | 6.0 | 0.3998834877 | 0.6403564476 | 0.4953570190 |
| H | 1.0 | 1.7078673726 | 2.4061348792 | 0.3312343941 |
| H | 1.0 | -1.3519631499 | 1.9683603244 | 0.1774713313 |
| H | 1.0 | -0.4257458321 | 2.3031860238 | 1.6935095067 |
| S | 16.0 | -0.2075994762 | -0.6156591847 | -0.6063148212 |
| H | 1.0 | 0.9684955616 | 0.2431547443 | 1.3192441427 |
| O | 8.0 | 0.9302466163 | -1.5009369029 | -0.9624412791 |
| C | 6.0 | -1.1980147061 | -1.5250409648 | 0.5822702391 |
| H | 1.0 | -0.5650646872 | -1.8755436580 | 1.3881082474 |
| H | 1.0 | -1.6208118479 | -2.3770655619 | 0.0662776957 |
| H | 1.0 | -1.9914920503 | -0.8946391072 | 0.9634919323 |

| | |
|---|---|
| Energy | -628.4188742 Hartree |
| ZPE | 0.122670 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.7553505468 | 2.0550927334 | -1.1594549075 |
| C | 6.0 | 0.8399702109 | 1.9379110079 | -0.0876880374 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.4327890072 | 1.8579035765 | 0.7015297005 |
| C | 6.0 | 0.4090834583 | 0.6269082911 | 0.5012449939 |
| H | 1.0 | 1.6980833084 | 2.4210274126 | 0.3553689453 |
| H | 1.0 | -1.3628570292 | 1.9253945567 | 0.1526878700 |
| H | 1.0 | -0.4621356295 | 2.2814336126 | 1.6946628518 |
| S | 16.0 | -0.1963892996 | -0.6135733033 | -0.6338406929 |
| H | 1.0 | 0.9711843055 | 0.2252475780 | 1.3362911216 |
| O | 8.0 | 0.9414119001 | -1.5280908565 | -1.0237318415 |
| C | 6.0 | -1.1920844261 | -1.4952996541 | 0.5910621463 |
| H | 1.0 | -0.5435764282 | -1.8518203488 | 1.3895986684 |
| H | 1.0 | -1.6464865833 | -2.3465710983 | 0.0898581569 |
| H | 1.0 | -1.9630651070 | -0.8356515799 | 0.9840248237 |

Energy -629.3021037 Hartree
ZPE 0.118067 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -629.6569384 Hartree

**Transition State for Cyclopropyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.1660524850 | -0.4850796619 | 0.6361749514 |
| C | 6.0 | 0.1246094977 | 0.2067979890 | 2.1032035504 |
| C | 6.0 | -1.0095317575 | -0.5195336847 | 2.7703441479 |
| C | 6.0 | 0.4015035083 | -0.9699213274 | 2.7590074874 |
| H | 1.0 | 0.5365227870 | 1.1788431305 | 2.2942088261 |
| H | 1.0 | -1.7411624285 | -1.0140349953 | 2.1464373329 |
| H | 1.0 | -1.4072816132 | -0.2191707241 | 3.7313173833 |
| S | 16.0 | 0.7526643110 | -2.4252914635 | 1.1601304883 |
| H | 1.0 | 1.0412858449 | -1.3222200148 | 3.5435024898 |
| O | 8.0 | 0.2945100485 | -1.3759587467 | 0.0764491478 |
| C | 6.0 | 2.5403454908 | -2.2936361145 | 1.0908051370 |
| H | 1.0 | 2.8396047344 | -1.2709184322 | 1.2806151659 |
| H | 1.0 | 2.8871740569 | -2.6027902997 | 0.1142975269 |
| H | 1.0 | 2.9558698687 | -2.9497082436 | 1.8473626370 |

Energy -628.3228487 Hartree
ZPE 0.116519 Hartree/Molecule
Imaginary Frequency -689.69 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.1642702987 | -0.4616719856 | 0.7564775012 |
| C | 6.0 | 0.1470939228 | 0.1844538065 | 2.1351729929 |
| C | 6.0 | -1.0099669571 | -0.5345909318 | 2.7820582911 |
| C | 6.0 | 0.4227464251 | -0.9455611375 | 2.8384557470 |
| H | 1.0 | 0.5293763536 | 1.1898808383 | 2.0898182597 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.6954507348 | -1.0809163210 | 2.1383307461 |
| H | 1.0 | -1.4743647733 | -0.1428667307 | 3.6827807140 |
| S | 16.0 | 0.7414133442 | -2.5044890478 | 1.0950141709 |
| H | 1.0 | 1.0889307287 | -1.2923903501 | 3.6107993725 |
| O | 8.0 | 0.2807920616 | -1.3293815706 | 0.0937462537 |
| C | 6.0 | 2.5290371656 | -2.3105643391 | 1.0802960979 |
| H | 1.0 | 2.7934432058 | -1.3137837645 | 1.4283568251 |
| H | 1.0 | 2.9092106484 | -2.4627790659 | 0.0737474624 |
| H | 1.0 | 2.9556351446 | -3.0579619893 | 1.7488018376 |

| | |
|---|---|
| Energy | -629.2292439 Hartree |
| ZPE | 0.111597 Hartree/Molecule |
| Imaginary Frequency | -566.12 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -629.5758436 Hartree |

**Cyclopropene**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.8374378818 | 0.0000003362 | 1.3503654178 |
| C | 6.0 | -0.1304706336 | -0.0000055839 | 0.8636833286 |
| C | 6.0 | -0.2910685261 | 0.6380915150 | -0.4788872972 |
| C | 6.0 | -0.2910657688 | -0.6380618501 | -0.4788628527 |
| H | 1.0 | -0.9562359803 | 0.0000002840 | 1.5649187673 |
| H | 1.0 | -0.3539180091 | -1.5635017225 | -1.0073448445 |
| H | 1.0 | -0.3539164708 | 1.5634770221 | -1.0073307514 |

| | |
|---|---|
| Energy | -115.8305271 Hartree |
| ZPE | 0.060249 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.8441385290 | 0.0000002267 | 1.3523663057 |
| C | 6.0 | -0.1294265310 | -0.0000027278 | 0.8694159150 |
| C | 6.0 | -0.2905586092 | 0.6516908695 | -0.4784192148 |
| C | 6.0 | -0.2905570753 | -0.6516739650 | -0.4784055548 |
| H | 1.0 | -0.9619539823 | -0.0000000236 | 1.5678838225 |
| H | 1.0 | -0.3554402679 | -1.5808268140 | -1.0131538843 |
| H | 1.0 | -0.3554395702 | 1.5808124348 | -1.0131456213 |

| | |
|---|---|
| Energy | -116.2374553 Hartree |
| ZPE | 0.057511 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -116.3525105 Hartree |

**Cyclobutyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.5593713770 | 1.1706645300 | -1.3041235107 |
| C | 6.0 | 1.4844036337 | 1.2096628673 | -0.2237378408 |
| C | 6.0 | 2.1751902936 | 0.0703265781 | 0.5555736863 |
| C | 6.0 | 0.1267211426 | 0.7869145751 | 0.3911135377 |
| C | 6.0 | 0.8822819505 | -0.1449203748 | 1.3709814675 |
| H | 1.0 | 0.5306854870 | -1.1664253422 | 1.4289454596 |
| H | 1.0 | 0.9234169566 | 0.2748272536 | 2.3698909736 |
| H | 1.0 | 1.7790095335 | 2.1989720810 | 0.1071958091 |
| H | 1.0 | -0.4666879296 | 1.5843639262 | 0.8263109303 |
| S | 16.0 | -0.9308923912 | -0.0492876116 | -0.8065919862 |
| H | 1.0 | 3.0607920346 | 0.3418746425 | 1.1176920803 |
| H | 1.0 | 2.3970094930 | -0.7788258456 | -0.0761053285 |
| O | 8.0 | -0.2294463518 | -1.3009273826 | -1.2062394414 |
| C | 6.0 | -2.2598979239 | -0.5386530549 | 0.2973367831 |
| H | 1.0 | -1.8721812847 | -1.1391149194 | 1.1099119505 |
| H | 1.0 | -2.9522756071 | -1.1330738614 | -0.2842999002 |
| H | 1.0 | -2.7665831657 | 0.3401368126 | 0.6779552140 |

| | |
|---|---|
| Energy | -667.4611224 Hartree |
| ZPE | 0.153892 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.5570916782 | 1.3170422770 | -1.2718160067 |
| C | 6.0 | 1.4765841720 | 1.2449023337 | -0.1865085297 |
| C | 6.0 | 2.1171429110 | 0.0205625803 | 0.5005299227 |
| C | 6.0 | 0.1116217576 | 0.8136509741 | 0.3973543586 |
| C | 6.0 | 0.8626122559 | -0.1031772333 | 1.3908782339 |
| H | 1.0 | 0.4675310424 | -1.1077138558 | 1.5384305869 |
| H | 1.0 | 0.9766538917 | 0.3862475645 | 2.3579941653 |
| H | 1.0 | 1.8001499662 | 2.1880954108 | 0.2532546852 |
| H | 1.0 | -0.5387970471 | 1.5966649914 | 0.7947034201 |
| S | 16.0 | -0.8664297379 | -0.0973125711 | -0.8326609628 |
| H | 1.0 | 3.0738594018 | 0.1708712372 | 0.9976163884 |
| H | 1.0 | 2.1785269748 | -0.8220788422 | -0.1833009115 |
| O | 8.0 | -0.1137023313 | -1.3719145263 | -1.1614495609 |
| C | 6.0 | -2.2137966435 | -0.5528947331 | 0.2846056930 |
| H | 1.0 | -1.8183340678 | -1.1133552058 | 1.1293614112 |
| H | 1.0 | -2.8956839379 | -1.1850257004 | -0.2790761276 |
| H | 1.0 | -2.7341130381 | 0.3419501731 | 0.6218931181 |

| | |
|---|---|
| Energy | -668.4911582 Hartree |
| ZPE | 0.148102 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -668.8830955 Hartree |

**Transition State for Cyclobutyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .2065771877 | -.7898737966 | -.5156134424 |
| C | 6.0 | .0664602539 | -.4404313900 | .5024730190 |
| C | 6.0 | 1.2562745203 | -.7562801760 | 1.3961959126 |
| C | 6.0 | -.7694022602 | -1.4002094338 | 1.3950840489 |
| C | 6.0 | .4810615829 | -1.5490219741 | 2.2790253840 |
| H | 1.0 | .8218908430 | -2.4579326990 | 2.7509754526 |
| H | 1.0 | 3.2862584916 | -.4485906355 | 3.5366360311 |
| H | 1.0 | -.2515175847 | .5946790107 | .4702250611 |
| H | 1.0 | -1.6461614744 | -.9692770195 | 1.8664790996 |
| H | 1.0 | -1.0670318005 | -2.3015766150 | .8695478388 |
| S | 16.0 | 1.6142115538 | 1.0735514113 | 2.7395503840 |
| H | 1.0 | 2.2764557122 | -.8708969752 | 1.0732589780 |
| O | 8.0 | .6300109071 | .4772625513 | 3.787300773 4 |
| C | 6.0 | 3.2295828204 | .6218040878 | 3.3822351389 |
| H | 1.0 | 3.3991081298 | 1.1287188788 | 4.3226132043 |
| H | 1.0 | 3.9812132156 | .9313649473 | 2.6644201876 |
| H | 1.0 | .3853036805 | -.5974562655 | 3.2851904386 |

Energy -667.3807965 Hartree
ZPE 0.146973 Hartree/Molecule
Imaginary Frequency -1784.64 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.2080111491 | -0.8322364236 | -0.5189429849 |
| C | 6.0 | 0.0989077460 | -0.4458211905 | 0.4956510456 |
| C | 6.0 | 1.2879129447 | -0.7518485515 | 1.3921234072 |
| C | 6.0 | -0.7468898024 | -1.3702380758 | 1.4193723703 |
| C | 6.0 | 0.5162191861 | -1.5487452553 | 2.2701829388 |
| H | 1.0 | 0.8358743871 | -2.4397412121 | 2.8006895959 |
| H | 1.0 | 3.2388428087 | -0.4748854009 | 3.4181997805 |
| H | 1.0 | -0.2156644959 | 0.5975291299 | 0.4345203023 |
| H | 1.0 | -1.6051957928 | -0.9087463981 | 1.9089755681 |
| H | 1.0 | -1.0770267096 | -2.2777912288 | 0.9137238440 |
| S | 16.0 | 1.5700418404 | 1.1129304635 | 2.7537372234 |
| H | 1.0 | 2.3226457051 | -0.8592608405 | 1.0824507209 |
| O | 8.0 | 0.5836802997 | 0.4470191487 | 3.8037060604 |
| C | 6.0 | 3.1907570587 | 0.6106807101 | 3.3556020009 |
| H | 1.0 | 3.3683336863 | 1.0412504425 | 4.3374031190 |
| H | 1.0 | 3.9429649999 | 0.9716596143 | 2.6545697935 |
| H | 1.0 | 0.3808807677 | -0.6259210248 | 3.2836327242 |

Energy -668.4355725 Hartree

| | |
|---|---|
| ZPE | 0.141434 Hartree/Molecule |
| Imaginary Frequency | -1071.97 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -668.8224824 Hartree |

**Cyclobutene**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .6048731984 | 1.8984761703 | .3328172109 |
| C | 6.0 | -.1109987773 | 1.0901636553 | .4333240652 |
| C | 6.0 | .1907154314 | .0004704354 | 1.4954062743 |
| C | 6.0 | -.0694886195 | -.0000908604 | -.6233765446 |
| C | 6.0 | -.1109587129 | -1.0897884552 | .4338958615 |
| H | 1.0 | .6049299553 | -1.8981380691 | .3338084260 |
| H | 1.0 | -1.1028039286 | -1.5185482719 | .5471985058 |
| H | 1.0 | -1.1028519385 | 1.5189652579 | .5464068094 |
| H | 1.0 | .1365297660 | -.9190902226 | -2.4880323703 |
| C | 6.0 | .0739463338 | -.0004512525 | -1.9297288917 |
| H | 1.0 | -.4303573706 | .0006895523 | 2.3830270832 |
| H | 1.0 | 1.2313224912 | .0005691221 | 1.7988004019 |
| H | 1.0 | .1364721714 | .9178629383 | -2.4885668316 |

| | |
|---|---|
| Energy | -193.9558175 Hartree |
| ZPE | 0.122758 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .4698677063 | 1.9578984513 | .3229845579 |
| C | 6.0 | -.1729355620 | 1.0857992833 | .4402653290 |
| C | 6.0 | .2392704749 | .0004677366 | 1.4689360337 |
| C | 6.0 | -.0977785930 | -.0001049516 | -.6159329508 |
| C | 6.0 | -.1728997367 | -1.0854351502 | .4408478831 |
| H | 1.0 | .4699339921 | -1.9575786744 | .3240442169 |
| H | 1.0 | -1.1988879834 | -1.4216933309 | .6054955506 |
| H | 1.0 | -1.1989373066 | 1.4221121955 | .6047278169 |
| H | 1.0 | .2565684782 | -.9249528035 | -2.4769138067 |
| C | 6.0 | .1514982808 | -.0004463196 | -1.9254273169 |
| H | 1.0 | -.2670964303 | .0007183705 | 2.4328226925 |
| H | 1.0 | 1.3161988682 | .0005287929 | 1.6305317012 |
| H | 1.0 | .2565278116 | .9237764000 | -2.4774017074 |

| | |
|---|---|
| Energy | -194.6466344 Hartree |
| ZPE | 0.118068 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -194.8398215 Hartree |

**Cyclopentyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.3312054866 | -0.0723465923 | -2.1174716215 |
| C | 6.0 | 1.3644115465 | -0.0975907390 | -1.0337635074 |
| C | 6.0 | 2.4407897522 | 0.8030811817 | -0.4274277365 |
| C | 6.0 | 2.0228095942 | 0.9154249400 | 1.0450962058 |
| C | 6.0 | 0.4754960307 | 0.8547892635 | 1.0423214405 |
| C | 6.0 | 0.0750026171 | 0.4353901064 | -0.3909768553 |
| H | 1.0 | 1.5251686271 | -1.1265577365 | -0.7240060272 |
| H | 1.0 | 2.4133736494 | 1.7804754765 | -0.9044096564 |
| H | 1.0 | 3.4427565321 | 0.4074561201 | -0.5536204961 |
| H | 1.0 | 2.4205137590 | 0.0734868706 | 1.6022151245 |
| H | 1.0 | 2.3982111600 | 1.8173723165 | 1.5159483686 |
| H | 1.0 | 0.0358238237 | 1.8124260171 | 1.2978473499 |
| H | 1.0 | 0.1221072154 | 0.1217578294 | 1.7564136377 |
| H | 1.0 | -0.2902630037 | 1.2846859071 | -0.9622485477 |
| S | 16.0 | -1.2388104888 | -0.8098799340 | -0.4684891726 |
| O | 8.0 | -0.9141405971 | -1.8498382490 | 0.5473617983 |
| C | 6.0 | -2.5918707232 | 0.1581208175 | 0.2085110783 |
| H | 1.0 | -2.3527147387 | 0.4876562113 | 1.2109452566 |
| H | 1.0 | -3.4573369730 | -0.4902656590 | 0.2463225145 |
| H | 1.0 | -2.8011838265 | 1.0037906153 | -0.4357853879 |

Energy -706.5299576 Hartree
ZPE 0.185889 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.3425031103 | -0.0879346393 | -2.1268257759 |
| C | 6.0 | 1.3630349109 | -0.0928799241 | -1.0370383899 |
| C | 6.0 | 2.4257611343 | 0.8159021749 | -0.4250724859 |
| C | 6.0 | 1.9996069998 | 0.8987088773 | 1.0446347652 |
| C | 6.0 | 0.4542306363 | 0.8499352927 | 1.0225627055 |
| C | 6.0 | 0.0711022253 | 0.4419816041 | -0.4133203964 |
| H | 1.0 | 1.5187809169 | -1.1209033331 | -0.6980766643 |
| H | 1.0 | 2.3750497550 | 1.8031482507 | -0.8912562215 |
| H | 1.0 | 3.4404409752 | 0.4393735148 | -0.5548784959 |
| H | 1.0 | 2.3858033800 | 0.0312201427 | 1.5814759160 |
| H | 1.0 | 2.3805145106 | 1.7882926296 | 1.5456707417 |
| H | 1.0 | 0.0116133836 | 1.8097732584 | 1.2872254493 |
| H | 1.0 | 0.0881392402 | 0.0964318031 | 1.7222128927 |
| H | 1.0 | -0.3084742287 | 1.2876078974 | -0.9943326370 |
| S | 16.0 | -1.2249656160 | -0.8426091319 | -0.4632856156 |
| O | 8.0 | -0.8619261544 | -1.8672010947 | 0.5940471760 |
| C | 6.0 | -2.5578290469 | 0.1753936841 | 0.2154805304 |
| H | 1.0 | -2.2873471978 | 0.5176556744 | 1.2119940085 |
| H | 1.0 | -3.4429255713 | -0.4529926359 | 0.2793601307 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.7517639203 | 1.0185307181 | -0.4457938673 |

Energy -707.7066255 Hartree
ZPE 0.178889 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -708.1372683 Hartree

**Transition State for Cyclopentyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.1656837069 | 1.2483065179 | 3.8735508256 |
| C | 6.0 | -0.4491445009 | 0.8533456906 | 3.1614416990 |
| C | 6.0 | -1.1170113368 | 0.4083116018 | 1.8502695904 |
| C | 6.0 | 0.0177875540 | 0.4917435236 | 0.8186780866 |
| C | 6.0 | 0.8617113045 | 1.6385352975 | 1.3282775381 |
| C | 6.0 | 0.5693878863 | 1.8968553967 | 2.6878814341 |
| H | 1.0 | 0.0487680914 | 0.0093643817 | 3.6373301810 |
| H | 1.0 | -1.9057187220 | 1.1062304302 | 1.5851926027 |
| H | 1.0 | -1.5576107842 | -0.5807031872 | 1.9062532092 |
| H | 1.0 | 0.6362354902 | -0.4050173096 | 0.8678964740 |
| H | 1.0 | -0.3156384788 | 0.6007197839 | -0.2063486535 |
| S | 16.0 | -0.1271273223 | 3.5593072545 | 0.4066694619 |
| H | 1.0 | 1.8265699997 | 1.8249893988 | 0.8911522270 |
| H | 1.0 | -0.1148329970 | 3.0435303618 | 2.4978481558 |
| H | 1.0 | 1.3814305896 | 2.1795593302 | 3.3423216415 |
| O | 8.0 | -0.6323639683 | 3.9572515030 | 1.8205177761 |
| C | 6.0 | 1.3617228439 | 4.5438005381 | 0.1970047058 |
| H | 1.0 | 1.8393867181 | 4.2486827040 | -0.7311553161 |
| H | 1.0 | 2.0389266515 | 4.3828789284 | 1.0268743801 |
| H | 1.0 | 1.0992307419 | 5.5921941520 | 0.1487725768 |

Energy -706.4587639 Hartree
ZPE 0.179027 Hartree/Molecule
Imaginary Frequency -1777.59 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.1387958151 | 1.2756285272 | 3.8730562057 |
| C | 6.0 | -0.4297367608 | 0.8791876928 | 3.1452725189 |
| C | 6.0 | -1.1021544980 | 0.4654980998 | 1.8298687137 |
| C | 6.0 | 0.0490026270 | 0.4972867995 | 0.8172290273 |
| C | 6.0 | 0.8875656025 | 1.6534028948 | 1.3125876378 |
| C | 6.0 | 0.6023532204 | 1.8995389778 | 2.6729547474 |
| H | 1.0 | 0.0674214452 | 0.0173748451 | 3.6019713874 |
| H | 1.0 | -1.8504292810 | 1.2131961157 | 1.5575819924 |
| H | 1.0 | -1.5990252425 | -0.5027661054 | 1.8836471895 |
| H | 1.0 | 0.6376675607 | -0.4240331043 | 0.8943529426 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.2801045096 | 0.5914467196 | -0.2192374569 |
| S | 16.0 | -0.1840709789 | 3.5165006668 | 0.3944471451 |
| H | 1.0 | 1.8658782329 | 1.8388905014 | 0.8799634542 |
| H | 1.0 | -0.1347390129 | 3.0335283606 | 2.5077629284 |
| H | 1.0 | 1.3893856544 | 2.2351842317 | 3.3413133645 |
| O | 8.0 | -0.6925089489 | 3.9017423876 | 1.8455390294 |
| C | 6.0 | 1.3251984521 | 4.4850715662 | 0.2226662042 |
| H | 1.0 | 1.8028290542 | 4.2100249518 | -0.7175874764 |
| H | 1.0 | 1.9953170206 | 4.2682937403 | 1.0521877867 |
| H | 1.0 | 1.0849722316 | 5.5448884291 | 0.2148512539 |

| | |
|---|---|
| Energy | -707.6612028 Hartree |
| ZPE | 0.172682 Hartree/Molecule |
| Imaginary Frequency | -1056.96 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -708.0864450 Hartree |

**Cyclopentene**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.1495995405 | 0.0000011635 | 0.4344450670 |
| C | 6.0 | -1.2174079946 | -0.0000331358 | -0.1191620716 |
| C | 6.0 | -0.3374615016 | 1.2306299253 | 0.1953307534 |
| C | 6.0 | 1.0604856742 | 0.6593625934 | 0.1730278570 |
| C | 6.0 | 1.0604798988 | -0.6593620538 | 0.1730347459 |
| C | 6.0 | -0.3374740246 | -1.2305635220 | 0.1953514558 |
| H | 1.0 | -1.4691511904 | 0.0000031820 | -1.1748365348 |
| H | 1.0 | -0.5617943631 | 1.6510195680 | 1.1746723889 |
| H | 1.0 | -0.4775052469 | 2.0312876948 | -0.5254287670 |
| H | 1.0 | -0.5617912095 | -1.6510249682 | 1.1746662610 |
| H | 1.0 | 1.9417629823 | 1.2764828688 | 0.1900785860 |
| H | 1.0 | 1.9417757914 | -1.2764919422 | 0.1900848914 |
| H | 1.0 | -0.4775099745 | -2.0313113745 | -0.5254515742 |

| | |
|---|---|
| Energy | -193.9902341 Hartree |
| ZPE | 0.124831 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.1783619701 | -0.0000014107 | 0.3402000231 |
| C | 6.0 | -1.2044559378 | 0.0000031374 | -0.1482340158 |
| C | 6.0 | -0.3437228759 | 1.2231839325 | 0.2208127955 |
| C | 6.0 | 1.0570169742 | 0.6705540457 | 0.1445649000 |
| C | 6.0 | 1.0570120280 | -0.6705429998 | 0.1445468994 |
| C | 6.0 | -0.3437358937 | -1.2231969146 | 0.2208734214 |
| H | 1.0 | -1.3723285972 | 0.0000014792 | -1.2261132908 |
| H | 1.0 | -0.5597141735 | 1.5740551255 | 1.2353513643 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.5112379673 | 2.0686679271 | -0.4483362819 |
| H | 1.0 | -0.5597098684 | -1.5740421914 | 1.2353201176 |
| H | 1.0 | 1.9426381201 | 1.2918432833 | 0.1425894095 |
| H | 1.0 | 1.9426455499 | -1.2918492633 | 0.1425845273 |
| H | 1.0 | -0.5112360874 | -2.0686761508 | -0.4483468106 |

Energy -194.6826303 Hartree
ZPE 0.119982 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -194.8746591 Hartree

**Cyclohexyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.0617573049 | 0.1306693465 | -0.0451634659 |
| C | 6.0 | -0.0369174779 | 0.0370349799 | 1.0324178485 |
| C | 6.0 | 0.1285501719 | 1.3760550612 | 3.2095605733 |
| C | 6.0 | -1.6483842530 | -0.4486107015 | 2.9160823367 |
| C | 6.0 | -1.2760750261 | 0.8789620977 | 3.5867048169 |
| C | 6.0 | -1.4612123557 | -0.3860362184 | 1.3985252538 |
| C | 6.0 | 0.3402205846 | 1.3680446059 | 1.6885072953 |
| S | 16.0 | 1.4392664228 | 0.3858781510 | 4.0137192233 |
| H | 1.0 | -1.0360889093 | -1.2508836882 | 3.3204507266 |
| H | 1.0 | -1.9798933653 | 1.6460083938 | 3.2708879304 |
| H | 1.0 | -2.1686923389 | 0.3273969737 | 0.9773943844 |
| H | 1.0 | -0.2863903126 | 2.1575122137 | 1.2775983101 |
| H | 1.0 | 0.6640127073 | -0.7375299264 | 1.3366765128 |
| H | 1.0 | 0.2731683911 | 2.3904591158 | 3.5685727321 |
| H | 1.0 | -2.6788433115 | -0.6930747757 | 3.1586840514 |
| H | 1.0 | -1.3870534897 | 0.7972605342 | 4.6642942421 |
| H | 1.0 | -1.6921261155 | -1.3513218716 | 0.9569647784 |
| H | 1.0 | 1.3682988435 | 1.6276208382 | 1.4717441914 |
| O | 8.0 | 2.7329021115 | 0.8322632312 | 3.4220883048 |
| C | 6.0 | 1.3748253569 | 1.1268427549 | 5.6482596290 |
| H | 1.0 | 2.1544871380 | 0.6594077819 | 6.2351895799 |
| H | 1.0 | 0.4161014760 | 0.9509392440 | 6.1182738197 |
| H | 1.0 | 1.5772667470 | 2.1876708583 | 5.5680657249 |

Energy -745.5718900 Hartree
ZPE 0.217125 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.1159669428 | 0.1637205050 | -0.0174675302 |
| C | 6.0 | -0.0155081681 | 0.0662641327 | 1.0619372511 |
| C | 6.0 | 0.0800732608 | 1.3667126057 | 3.2440290458 |
| C | 6.0 | -1.6422358025 | -0.4767162358 | 2.9008401025 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -1.3130282669 | 0.8432008620 | 3.6005491297 |
| C | 6.0 | -1.4409936582 | -0.3712626516 | 1.3906796034 |
| C | 6.0 | 0.3257987089 | 1.3928828631 | 1.7370707414 |
| S | 16.0 | 1.3747959281 | 0.3060233137 | 4.0203488570 |
| H | 1.0 | -0.9996097151 | -1.2694400631 | 3.2919166738 |
| H | 1.0 | -2.0374157443 | 1.6036620026 | 3.2933459421 |
| H | 1.0 | -2.1462443860 | 0.3602062077 | 0.9825759077 |
| H | 1.0 | -0.2986388864 | 2.1861993555 | 1.3151544607 |
| H | 1.0 | 0.6893626085 | -0.7028908124 | 1.3904610056 |
| H | 1.0 | 0.2269443853 | 2.3735414679 | 3.6465056126 |
| H | 1.0 | -2.6704879631 | -0.7623914760 | 3.1318077790 |
| H | 1.0 | -1.4227462643 | 0.7354945089 | 4.6834252454 |
| H | 1.0 | -1.6666573500 | -1.3275164417 | 0.9145093254 |
| H | 1.0 | 1.3677011974 | 1.6605488852 | 1.5579385825 |
| O | 8.0 | 2.6885338895 | 0.6098138354 | 3.3255822512 |
| C | 6.0 | 1.4018072213 | 1.1871749063 | 5.6006103496 |
| H | 1.0 | 2.0820513139 | 0.6595205793 | 6.2646789465 |
| H | 1.0 | 0.4053668531 | 1.2131633917 | 6.0376249168 |
| H | 1.0 | 1.7743441957 | 2.1946572579 | 5.4213746002 |

| | |
|---|---|
| Energy | -746.8959349 Hartree |
| ZPE | 0.209104 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -747.3660964 Hartree |

**Transition State for Cyclohexyl Methyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.1700434230 | 0.3401053137 | -0.8748603218 |
| S | 16.0 | -1.5592193037 | 0.8141352227 | 0.7018168133 |
| O | 8.0 | -0.5270062368 | 0.6621845314 | 1.8470497208 |
| C | 6.0 | -1.6886162663 | 2.5921974986 | 0.4754948307 |
| C | 6.0 | 2.1397725925 | -0.8536202531 | 0.2317232112 |
| C | 6.0 | 0.8067546563 | -2.0254870811 | -1.5334538523 |
| C | 6.0 | 1.4286165891 | -2.1524192710 | -0.1444159661 |
| C | 6.0 | -0.2905554063 | -0.9565057145 | -1.5317133326 |
| C | 6.0 | 1.2489454840 | 0.3785517419 | 0.0447454184 |
| H | 1.0 | 3.0277590922 | -0.7527382920 | -0.3915022939 |
| H | 1.0 | 1.5814474158 | -1.7643366849 | -2.2518922836 |
| H | 1.0 | 0.6508744602 | -2.3751710574 | 0.5839209192 |
| H | 1.0 | -1.1568979928 | -1.3537184791 | -1.0160594264 |
| H | 1.0 | 0.5389316376 | 0.5048613381 | 1.1406168825 |
| H | 1.0 | -0.0446748509 | 1.2362824286 | -1.4290511072 |
| H | 1.0 | 2.4911147734 | -0.9043124646 | 1.2579458714 |
| H | 1.0 | 0.3811951664 | -2.9702782606 | -1.8593288163 |
| H | 1.0 | 2.1327729903 | -2.9791327036 | -0.1169456290 |
| H | 1.0 | -0.6150809026 | -0.7375866734 | -2.5450236866 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.7982981065 | 1.3119010461 | 0.0268086651 |
| H | 1.0 | -0.7117768146 | 3.0230691615 | 0.2926916113 |
| H | 1.0 | -2.1129573267 | 3.0403495364 | 1.3640970023 |
| H | 1.0 | -2.3392627865 | 2.7842997165 | -0.3708247304 |

Energy -745.4938101 Hartree
ZPE 0.210195 Hartree/Molecule
Imaginary Frequency -1707.62 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.1600401556 | 0.3787407351 | -0.8850457883 |
| S | 16.0 | -1.5082429728 | 0.6952095856 | 0.7342666487 |
| O | 8.0 | -0.4128734086 | 0.5825673950 | 1.8647183794 |
| C | 6.0 | -1.6691746480 | 2.4721900683 | 0.4873630582 |
| C | 6.0 | 2.1315506791 | -0.8202018140 | 0.2116634452 |
| C | 6.0 | 0.7767939543 | -2.0092286599 | -1.4967706724 |
| C | 6.0 | 1.3466517443 | -2.0920797165 | -0.0853222120 |
| C | 6.0 | -0.2750074644 | -0.9029404622 | -1.5834663208 |
| C | 6.0 | 1.2731379575 | 0.4186541775 | -0.0083277325 |
| H | 1.0 | 3.0012074848 | -0.7850684883 | -0.4532116559 |
| H | 1.0 | 1.5955394278 | -1.7981767205 | -2.1906241305 |
| H | 1.0 | 0.5319379077 | -2.1982700363 | 0.6378261579 |
| H | 1.0 | -1.2085419271 | -1.2811060196 | -1.1571924561 |
| H | 1.0 | 0.6182143938 | 0.5135712289 | 1.1385955586 |
| H | 1.0 | -0.0709050683 | 1.2934100518 | -1.4250555296 |
| H | 1.0 | 2.5197500396 | -0.8383610033 | 1.2326333281 |
| H | 1.0 | 0.3354156087 | -2.9595683974 | -1.8040153299 |
| H | 1.0 | 1.9912885016 | -2.9663355379 | 0.0235695420 |
| H | 1.0 | -0.4954913422 | -0.6759271114 | -2.6298206900 |
| H | 1.0 | 1.8212937533 | 1.3591764357 | -0.0064816642 |
| H | 1.0 | -0.6914548917 | 2.9015260249 | 0.2771501420 |
| H | 1.0 | -2.0860008462 | 2.9340171221 | 1.3785321333 |
| H | 1.0 | -2.3346505387 | 2.6408317426 | -0.3591447111 |

Energy -746.8417694 Hartree
ZPE 0.202610 Hartree/Molecule
Imaginary Frequency -1016.76 $cm^{-1}$
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -747.3062788 Hartree

**Cyclohexene**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.1699721818 | 0.2135597656 | -2.2384951215 |
| C | 6.0 | 0.6505404510 | 0.1135064489 | -1.2987544217 |
| C | 6.0 | 0.7211244169 | -0.2541040633 | 1.1912672431 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -1.4763829634 | -0.2457820935 | -0.0432014649 |
| C | 6.0 | -0.7210920035 | 0.2541242359 | 1.1912276681 |
| C | 6.0 | -0.6505089757 | -0.1135018954 | -1.2987282951 |
| C | 6.0 | 1.4763055224 | 0.2457892807 | -0.0432045858 |
| H | 1.0 | 0.7158719288 | -1.3424142782 | 1.1921925505 |
| H | 1.0 | -1.7627612194 | -1.2890475417 | 0.0902710580 |
| H | 1.0 | -0.7158735744 | 1.3424053543 | 1.1921949058 |
| H | 1.0 | -1.1699842733 | -0.2135616913 | -2.2385112315 |
| H | 1.0 | 1.7627675130 | 1.2890558323 | 0.0902728835 |
| H | 1.0 | 2.4064996524 | -0.3056061298 | -0.1604473522 |
| H | 1.0 | 1.2359426975 | 0.0586884351 | 2.0953153646 |
| H | 1.0 | -2.4064651675 | 0.3055862584 | -0.1604436262 |
| H | 1.0 | -1.2359561866 | -0.0586979179 | 2.0953360033 |

Energy -233.0354408 Hartree
ZPE 0.156215 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.1777934289 | 0.2281672536 | -2.2395874314 |
| C | 6.0 | 0.6601210177 | 0.1201737314 | -1.2925606459 |
| C | 6.0 | 0.7146082368 | -0.2674264959 | 1.1822048621 |
| C | 6.0 | -1.4758639202 | -0.2527526232 | -0.0358465010 |
| C | 6.0 | -0.7145998003 | 0.2674408647 | 1.1821871413 |
| C | 6.0 | -0.6601155670 | -0.1201709461 | -1.2925398882 |
| C | 6.0 | 1.4758623076 | 0.2527350393 | -0.0358455762 |
| H | 1.0 | 0.6844366143 | -1.3600113299 | 1.1476671300 |
| H | 1.0 | -1.7481103686 | -1.3029898746 | 0.1167977997 |
| H | 1.0 | -0.6844362957 | 1.3600035773 | 1.1476673532 |
| H | 1.0 | -1.1777984765 | -0.2281662600 | -2.2395984921 |
| H | 1.0 | 1.7481128372 | 1.3029986559 | 0.1167988828 |
| H | 1.0 | 2.4191383037 | -0.2874378145 | -0.1514499037 |
| H | 1.0 | 1.2346092407 | 0.0102016308 | 2.1009182373 |
| H | 1.0 | -2.4191421277 | 0.2874391625 | -0.1514501698 |
| H | 1.0 | -1.2346154309 | -0.0102045712 | 2.1009287800 |

Energy -233.8722947 Hartree
ZPE 0.150356 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -234.1032765 Hartree

**Methyl 1-Methylcyclopropyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .1190990719 | .0323003270 | -2.7630698290 |
| C | 6.0 | .1756536823 | .6145498930 | -1.8599038352 |
| C | 6.0 | -1.0805926354 | 1.1948649028 | -1.2941972344 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.4357627934 | .0155224846 | -.6277557910 |
| H | 1.0 | 1.0793772790 | 1.1923888612 | -1.7635197642 |
| H | 1.0 | -2.0093312191 | 1.0170513812 | -1.8063576715 |
| H | 1.0 | -1.0161273756 | 2.1556712464 | -.8145134426 |
| C | 6.0 | -1.1233702243 | -1.3328741010 | -.6754113529 |
| S | 16.0 | .3861826674 | .4155967433 | .9162146465 |
| H | 1.0 | -.4095959005 | -2.1493648265 | -.7051644936 |
| H | 1.0 | -1.7400915576 | -1.4027416057 | -1.5651562600 |
| H | 1.0 | -1.7552759927 | -1.4560340545 | .1950737386 |
| O | 8.0 | -.5174009536 | .0084576372 | 2.0249940575 |
| C | 6.0 | 1.7076922955 | -.7997397294 | .8812558542 |
| H | 1.0 | 1.2944807656 | -1.7986829856 | .9148460289 |
| H | 1.0 | 2.3069712272 | -.6378285579 | 1.7677286175 |
| H | 1.0 | 2.3186323993 | -.6623476752 | -.0019467789 |

Energy -667.4590534 Hartree
ZPE 0.152432 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .1627100927 | .0236709794 | -2.7545764782 |
| C | 6.0 | .2017321563 | .6102116024 | -1.8469105119 |
| C | 6.0 | -1.0744607839 | 1.1908095653 | -1.3044347453 |
| C | 6.0 | -.4360391592 | .0103834091 | -.6256195473 |
| H | 1.0 | 1.1052196846 | 1.1942726514 | -1.7252304064 |
| H | 1.0 | -1.9950300864 | 1.0072119962 | -1.8403097591 |
| H | 1.0 | -1.0166047788 | 2.1547591415 | -.8170625067 |
| C | 6.0 | -1.1134532830 | -1.3341013567 | -.6583426271 |
| S | 16.0 | .3591260014 | .4314612946 | .9378064228 |
| H | 1.0 | -.3935768994 | -2.1505817899 | -.7092144247 |
| H | 1.0 | -1.7629704057 | -1.4019416005 | -1.5305456130 |
| H | 1.0 | -1.7169032096 | -1.4527831520 | .2411011548 |
| O | 8.0 | -.5599510756 | -.0034831873 | 2.0596760777 |
| C | 6.0 | 1.6887006640 | -.7916946035 | .8494926765 |
| H | 1.0 | 1.2627957860 | -1.7920477187 | .8759383102 |
| H | 1.0 | 2.3155330992 | -.6492118672 | 1.7266689790 |
| H | 1.0 | 2.2737129334 | -.6401454229 | -.0553205115 |

Energy -668.4919571 Hartree
ZPE 0.146771 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -668.8852587 Hartree

**Transition State for Methyl 1-Methylcyclopropyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .3676395469 | .2138190075 | -2.8589619969 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .3776263571 | .6718913836 | -1.8848855006 |
| C | 6.0 | -.8505774066 | 1.4276566024 | -1.4220085972 |
| C | 6.0 | -.5349998039 | .0919085621 | -.8743621707 |
| H | 1.0 | 1.3355329091 | 1.0671476996 | -1.5954519972 |
| H | 1.0 | -1.6991170337 | 1.4871788683 | -2.0814708566 |
| H | 1.0 | -.6904213096 | 2.3053563431 | -.8215059176 |
| C | 6.0 | -1.2693591977 | -1.0977268060 | -.7410089365 |
| S | 16.0 | .3509195729 | .3301903629 | 1.1214919340 |
| H | 1.0 | -.8608538341 | -1.9858004899 | -1.1991698678 |
| H | 1.0 | -2.3441688543 | -1.0105923936 | -.7794107834 |
| H | 1.0 | -1.0212163860 | -1.2066518893 | .7067544102 |
| O | 8.0 | -.5411739474 | -.8213170918 | 1.6758194844 |
| C | 6.0 | 1.9296838675 | -.4855864513 | .8681155720 |
| H | 1.0 | 2.2868079582 | -.8556767165 | 1.8194996040 |
| H | 1.0 | 2.6358412619 | .2352626189 | .4743468422 |
| H | 1.0 | 1.8148087998 | -1.3090877101 | .1753964777 |

| | |
|---|---|
| Energy | -667.3724596 Hartree |
| ZPE | 0.145690 Hartree/Molecule |
| Imaginary Frequency | -1552.12 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .4124176026 | .1946501009 | -2.8535302095 |
| C | 6.0 | .3987940011 | .6412428056 | -1.8675608891 |
| C | 6.0 | -.8437819310 | 1.4198848955 | -1.4388104986 |
| C | 6.0 | -.5517105179 | .0827167560 | -.8774917850 |
| H | 1.0 | 1.3542710623 | 1.0375644708 | -1.5468976349 |
| H | 1.0 | -1.6668326460 | 1.5005657246 | -2.1370145197 |
| H | 1.0 | -.6769369308 | 2.3024233608 | -.8346944809 |
| C | 6.0 | -1.2795786335 | -1.0931899168 | -.7417354206 |
| S | 16.0 | .3498972673 | .3621020417 | 1.1886247418 |
| H | 1.0 | -.8631884331 | -2.0163911549 | -1.1278838598 |
| H | 1.0 | -2.3609871181 | -1.0341678534 | -.7073886937 |
| H | 1.0 | -1.0219141376 | -1.2004153326 | .7043514938 |
| O | 8.0 | -.5570299198 | -.8545349493 | 1.6886879070 |
| C | 6.0 | 1.9130119248 | -.4544641704 | .8348332757 |
| H | 1.0 | 2.2504876859 | -.9757101194 | 1.7266231435 |
| H | 1.0 | 2.6442708578 | .3038162185 | .5585257041 |
| H | 1.0 | 1.7857823661 | -1.1581209776 | .0145494258 |

| | |
|---|---|
| Energy | -668.4285263 Hartree |
| ZPE | 0.140583 Hartree/Molecule |
| Imaginary Frequency | -823.01 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -668.8159292 Hartree |

**Methylenecycloproane**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .7636173139 | .0000260178 | -.8811647934 |
| C | 6.0 | -.7636203412 | .0000144040 | -.8811659206 |
| H | 1.0 | 1.2656494405 | .9055473783 | -1.1798130705 |
| H | 1.0 | -1.2656533651 | -.9055586574 | -1.1798159442 |
| C | 6.0 | .0000072639 | -.0000282218 | .3651296528 |
| H | 1.0 | -1.2656502827 | .9055506696 | -1.1798143679 |
| H | 1.0 | 1.2656550243 | -.9055635379 | -1.1798179316 |
| C | 6.0 | -.0000438252 | .0000060824 | 1.6728930607 |
| H | 1.0 | -.9194699040 | .0000033642 | 2.2324785333 |
| H | 1.0 | .9195086751 | .0000025008 | 2.2324976956 |

Energy -154.8978904 Hartree
ZPE 0.091289 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .7685684141 | .0000171737 | -.8847862512 |
| C | 6.0 | -.7685721558 | .0000161870 | -.8847908337 |
| H | 1.0 | 1.2686764541 | .9104583518 | -1.1898413994 |
| H | 1.0 | -1.2686833452 | -.9104822889 | -1.1898676762 |
| C | 6.0 | .0000022393 | .0000145608 | .3629635459 |
| H | 1.0 | -1.2686745773 | .9104561352 | -1.1898400797 |
| H | 1.0 | 1.2686841270 | -.9104843918 | -1.1898686719 |
| C | 6.0 | -.0000052293 | -.0000062212 | 1.6890384183 |
| H | 1.0 | -.9251868618 | .0000052616 | 2.2491990903 |
| H | 1.0 | .9251909346 | .0000052317 | 2.2492007718 |

Energy -155.4447300 Hartree
ZPE 0.087625 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -155.5991864 Hartree

**Methyl 1-Cyclobutyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9145514429 | .3547115624 | -1.2885960660 |
| C | 6.0 | .9126374669 | -.1799273046 | 2.1038796242 |
| H | 1.0 | 1.1135157750 | -1.2417065560 | 2.0730843718 |
| C | 6.0 | .1682468652 | -.1810972230 | -.5893243559 |
| H | 1.0 | 1.6063785405 | 1.5582267751 | -.3371275722 |
| H | 1.0 | .6363608658 | .0957422771 | 3.1133387009 |
| H | 1.0 | 1.7820823770 | .3895280429 | 1.8012119217 |
| C | 6.0 | .6426053981 | -1.6219292954 | -.6970160366 |

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -.5004580142 | .2027223109 | 1.0624768782 |
| H | 1.0 | 1.5587248621 | -1.7913704219 | -.1408745688 |
| H | 1.0 | .8447033581 | -1.8609074822 | -1.7363071630 |
| H | 1.0 | -.1208077219 | -2.2974933212 | -.3294522561 |
| O | 8.0 | -1.5248045658 | -.8367210524 | 1.3614071703 |
| C | 6.0 | 1.0973853066 | .9583734657 | -1.0843891978 |
| C | 6.0 | -.8874233985 | .2906883544 | -1.6264271674 |
| C | 6.0 | -.1011511058 | 1.6052815552 | -1.8104483939 |
| H | 1.0 | -.5294391537 | 2.4268595560 | -1.2487641300 |
| H | 1.0 | .0674636821 | 1.9350475837 | -2.8282212988 |
| H | 1.0 | 1.8428528153 | .5716731233 | -1.7709583374 |
| H | 1.0 | -.8591057298 | -.3359406257 | -2.5104964474 |

Energy -706.4983490 Hartree
ZPE 0.183528 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9023106042 | .2479449887 | -1.3673327367 |
| C | 6.0 | .9077569544 | -.1582132684 | 2.0523805330 |
| H | 1.0 | 1.0615618792 | -1.2345243465 | 2.0480717988 |
| C | 6.0 | .1886010518 | -.1940664118 | -.6074304018 |
| H | 1.0 | 1.6852572622 | 1.5082197983 | -.3581219331 |
| H | 1.0 | .6715590128 | .1633441898 | 3.0639870895 |
| H | 1.0 | 1.7926889699 | .3667200127 | 1.6981881448 |
| C | 6.0 | .6435413029 | -1.6356658441 | -.6505996398 |
| S | 16.0 | -.5280462412 | .2400397631 | 1.0248948334 |
| H | 1.0 | 1.5719592466 | -1.7910409722 | -.1017853220 |
| H | 1.0 | .8130159603 | -1.9333294665 | -1.6854407453 |
| H | 1.0 | -.1326997256 | -2.2741506378 | -.2268420775 |
| O | 8.0 | -1.5871069447 | -.8022772077 | 1.3268382234 |
| C | 6.0 | 1.1103352731 | .9475627205 | -1.0974030157 |
| C | 6.0 | -.8519407924 | .2697307902 | -1.6581115395 |
| C | 6.0 | -.1208559634 | 1.6261988871 | -1.7347947631 |
| H | 1.0 | -.5636700884 | 2.3606977575 | -1.0640844936 |
| H | 1.0 | .0053961464 | 2.0770039231 | -2.7172578865 |
| H | 1.0 | 1.7987728263 | .5642999613 | -1.8522464912 |
| H | 1.0 | -.7285993459 | -.3067333130 | -2.5759139014 |

Energy -707.6788682 Hartree
ZPE 0.176997 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -708.1109383 Hartree

**Transition State for Methyl 1-Cyclobutyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.9896199718 | -.3789306412 | .7661602936 |
| H | 1.0 | 2.4014854462 | -.7741184566 | 1.6851570705 |
| H | 1.0 | 2.6597961269 | .3741813779 | .3683957664 |
| C | 6.0 | -.6595780692 | .1794187088 | -.9431088835 |
| C | 6.0 | -1.3373197653 | 1.5066526588 | -1.2585484272 |
| H | 1.0 | 1.8725510646 | -1.1839246858 | .0514185735 |
| C | 6.0 | .3528325264 | .4055837693 | -2.0605697221 |
| C | 6.0 | -1.3457510306 | -1.0272821308 | -.6719322248 |
| S | 16.0 | .4017037460 | .3837847759 | 1.1242081020 |
| H | 1.0 | -.9776192307 | -1.9107247110 | -1.1737663023 |
| H | 1.0 | -2.4233827931 | -.9594206139 | -.6314549518 |
| H | 1.0 | -1.0069054938 | -1.1557462579 | .6413101222 |
| O | 8.0 | -.4379815774 | -.8021896326 | 1.6769411917 |
| H | 1.0 | -.9449567460 | 2.3359269920 | -.6832719050 |
| H | 1.0 | -2.4188400238 | 1.5156201832 | -1.2088586931 |
| C | 6.0 | -.6662745236 | 1.4135235548 | -2.6520653991 |
| H | 1.0 | .6209296811 | -.4616317938 | -2.6511885876 |
| H | 1.0 | 1.2542218456 | .9120616542 | -1.7380546154 |
| H | 1.0 | -.2604110377 | 2.3303072136 | -3.0617960721 |
| H | 1.0 | -1.3147736175 | .9509453352 | -3.3855495359 |

| | |
|---|---|
| Energy | -706.4235054 Hartree |
| ZPE | 0.176990 Hartree/Molecule |
| Imaginary Frequency | -1763.84 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.9379791327 | -.3752401624 | .7064581357 |
| H | 1.0 | 2.3470515762 | -.8908648213 | 1.5713189515 |
| H | 1.0 | 2.6318531697 | .3993560519 | .3831973734 |
| C | 6.0 | -.6358090972 | .1977884866 | -.9041695371 |
| C | 6.0 | -1.3167592462 | 1.5162689261 | -1.2510719125 |
| H | 1.0 | 1.7767293389 | -1.0854925045 | -.1023623950 |
| C | 6.0 | .3919389648 | .4255369114 | -2.0086140811 |
| C | 6.0 | -1.3313100744 | -1.0028282123 | -.6909120456 |
| S | 16.0 | .3801050431 | .4000824635 | 1.1694427719 |
| H | 1.0 | -.9439675019 | -1.9034449904 | -1.1550304259 |
| H | 1.0 | -2.4119698355 | -.9538018187 | -.6134434750 |
| H | 1.0 | -1.0088163321 | -1.1602726526 | .6609922587 |
| O | 8.0 | -.4765482475 | -.8387603129 | 1.6807709006 |
| H | 1.0 | -.8899759150 | 2.3641608467 | -.7119101118 |
| H | 1.0 | -2.4036314015 | 1.5525423731 | -1.1824255492 |
| C | 6.0 | -.6634946679 | 1.3644567889 | -2.6463011167 |
| H | 1.0 | .7304840985 | -.4430103844 | -2.5736746383 |
| H | 1.0 | 1.2576485138 | 1.0028955785 | -1.6771021181 |
| H | 1.0 | -.2988368355 | 2.2676319910 | -3.1349021294 |
| H | 1.0 | -1.3133241831 | .8170327419 | -3.3268350561 |

| | |
|---|---|
| Energy | -707.6251729 Hartree |
| ZPE | 0.170736 Hartree/Molecule |
| Imaginary Frequency | -1056.23 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -708.0513096 Hartree |

**Methylenecyclobutane**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.8954785312 | 1.7335952297 | 0.3768696459 |
| C | 6.0 | 0.0174501509 | 1.0973800159 | 0.4251171049 |
| C | 6.0 | 0.0629106693 | 0.0005105970 | 1.5232748126 |
| C | 6.0 | -0.0258346190 | -0.0002581426 | -0.6259750353 |
| C | 6.0 | 0.0174580004 | -1.0972602131 | 0.4259463464 |
| H | 1.0 | 0.8955149837 | -1.7334268050 | 0.3782344443 |
| H | 1.0 | -0.8617338836 | -1.7331773661 | 0.4508082839 |
| H | 1.0 | -0.8618073354 | 1.7332870335 | 0.4494249720 |
| H | 1.0 | -0.1029663215 | -0.9186356732 | -2.5013218233 |
| C | 6.0 | -0.0797982058 | -0.0004157228 | -1.9391890085 |
| H | 1.0 | -0.7886095366 | 0.0007720678 | 2.1931127803 |
| H | 1.0 | 0.9670076250 | 0.0007399606 | 2.1202821943 |
| H | 1.0 | -0.1028145636 | 0.9179829724 | -2.5011121864 |

| | |
|---|---|
| Energy | -193.9554918 Hartree |
| ZPE | 0.122449 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .8997014917 | 1.7407546486 | .3820232279 |
| C | 6.0 | .0175418146 | 1.1006117040 | .4275090707 |
| C | 6.0 | .0629549429 | .0004914569 | 1.5239190726 |
| C | 6.0 | -.0255586335 | -.0002107412 | -.6196528161 |
| C | 6.0 | .0175524859 | -1.1003606863 | .4282334166 |
| H | 1.0 | .8997303052 | -1.7405212622 | .3832128415 |
| H | 1.0 | -.8655602209 | -1.7402056495 | .4561132319 |
| H | 1.0 | -.8655986766 | 1.7404289021 | .4549150508 |
| H | 1.0 | -.1034567041 | -.9245104667 | -2.5141822229 |
| C | 6.0 | -.0803192098 | -.0004167607 | -1.9520350861 |
| H | 1.0 | -.7927793265 | .0007229374 | 2.1964318640 |
| H | 1.0 | .9714426085 | .0007022982 | 2.1232463438 |
| H | 1.0 | -.1033953826 | .9236075733 | -2.5142614637 |

| | |
|---|---|
| Energy | -194.6453352 Hartree |
| ZPE | 0.117521 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -194.8378544 Hartree |

**Methyl 1-Methylcyclopentyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.8771661033 | -.2322665640 | -1.1591536439 |
| C | 6.0 | .7928390227 | -.5639995916 | 2.3054211077 |
| H | 1.0 | .8382396604 | -1.6416937505 | 2.2387234949 |
| C | 6.0 | .1951625386 | -.3860847969 | -.4542189048 |
| H | 1.0 | 2.1204188179 | .6245157449 | -.0359431167 |
| H | 1.0 | .4822838762 | -.2888325512 | 3.3048685661 |
| H | 1.0 | 1.7561213512 | -.1189538534 | 2.0955663050 |
| C | 6.0 | .4911869002 | -1.8816153371 | -.5263075680 |
| S | 16.0 | -.4759839134 | .0652224996 | 1.1995985187 |
| H | 1.0 | 1.3698472324 | -2.1523754769 | .0489393266 |
| H | 1.0 | .6786923149 | -2.1644341379 | -1.5573442672 |
| H | 1.0 | -.3545253836 | -2.4522112953 | -.1619274414 |
| O | 8.0 | -1.6638116407 | -.8112115012 | 1.4198714790 |
| C | 6.0 | 1.3771678528 | .5278611737 | -.8204288111 |
| C | 6.0 | -.8800774950 | .0571201833 | -1.4668567820 |
| C | 6.0 | -.7022141477 | 1.5767419815 | -1.6356462869 |
| H | 1.0 | -1.3908071142 | 2.1169438660 | -.9959337379 |
| H | 1.0 | -.9158956214 | 1.8839965694 | -2.6532532908 |
| H | 1.0 | .7920927739 | 2.5810519054 | -.4054840079 |
| H | 1.0 | -.6703749698 | -.4490187574 | -2.4050960858 |
| H | 1.0 | 1.8821088903 | .0717116365 | -1.6677757524 |
| C | 6.0 | .7633887622 | 1.8802076511 | -1.2324012316 |
| H | 1.0 | 1.3250444293 | 2.3305469181 | -2.0430824654 |

Energy -745.5636986 Hartree
ZPE 0.215433 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.8477196639 | -0.2918300160 | -1.1906216641 |
| C | 6.0 | 0.7858030963 | -0.5587412899 | 2.2549525514 |
| H | 1.0 | 0.7575727650 | -1.6446766471 | 2.2103610910 |
| C | 6.0 | 0.2155832694 | -0.3887247485 | -0.4683646247 |
| H | 1.0 | 2.1399087802 | 0.6133111112 | -0.0381200237 |
| H | 1.0 | 0.5328951583 | -0.2377724758 | 3.2627432320 |
| H | 1.0 | 1.7691582575 | -0.1789364363 | 1.9874555846 |
| C | 6.0 | 0.4991946340 | -1.8791593443 | -0.4910764264 |
| S | 16.0 | -0.4942119869 | 0.1119191439 | 1.1659257111 |
| H | 1.0 | 1.3904759853 | -2.1376992935 | 0.0794648233 |
| H | 1.0 | 0.6562260608 | -2.2028639599 | -1.5205757115 |
| H | 1.0 | -0.3552124616 | -2.4210480411 | -0.0839806753 |
| O | 8.0 | -1.7263819188 | -0.7512399149 | 1.3747752104 |
| C | 6.0 | 1.3884407320 | 0.5269038052 | -0.8250912053 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.8509195490 | 0.0381028760 | -1.4852156086 |
| C | 6.0 | -0.7090864693 | 1.5637755243 | -1.5996050279 |
| H | 1.0 | -1.4002899839 | 2.0621225672 | -0.9199252895 |
| H | 1.0 | -0.9489210855 | 1.9120237753 | -2.6037857596 |
| H | 1.0 | 0.7862333880 | 2.5672731744 | -0.3629974771 |
| H | 1.0 | -0.6067820382 | -0.4411318249 | -2.4367702531 |
| H | 1.0 | 1.8888274401 | 0.0807513629 | -1.6890842707 |
| C | 6.0 | 0.7568652866 | 1.8787313308 | -1.2074649106 |
| H | 1.0 | 1.3060783373 | 2.3521318372 | -2.0208638716 |

| | |
|---|---|
| Energy | -746.8922794 Hartree |
| ZPE | .207735 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -747.3633189 Hartree |

**Transition State for Methyl 1-Methylcyclopentyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 2.3539528051 | -0.1681981168 | 0.7950514757 |
| H | 1.0 | 2.9843454341 | -0.0628478334 | 1.6682100254 |
| H | 1.0 | 2.8248939313 | 0.3238625308 | -0.0481904396 |
| C | 6.0 | -0.7918376670 | -0.5322886279 | -0.3968164762 |
| C | 6.0 | -1.6904541433 | 0.6483693391 | -0.6875508658 |
| H | 1.0 | 2.2225060557 | -1.2220166321 | 0.5821951925 |
| C | 6.0 | 0.0527130891 | -0.7317972964 | -1.6305927621 |
| C | 6.0 | -1.1359782662 | -1.5402679547 | 0.5342006231 |
| S | 16.0 | 0.7676181868 | 0.6096082485 | 1.1256671669 |
| H | 1.0 | -0.7435982202 | -2.5266098900 | 0.3290906603 |
| H | 1.0 | -2.1707042952 | -1.5425144298 | 0.8494626582 |
| H | 1.0 | -0.5289443527 | -1.0803592071 | 1.5961126242 |
| O | 8.0 | 0.1921506927 | -0.2567775778 | 2.2815582275 |
| H | 1.0 | -2.5936792837 | 0.2399334246 | -1.1394433195 |
| H | 1.0 | -1.9987111095 | 1.1712674327 | 0.2091951396 |
| C | 6.0 | -0.9310623687 | 1.5313913710 | -1.6977988288 |
| H | 1.0 | 0.9770299214 | -1.2651537721 | -1.4502370077 |
| H | 1.0 | -0.5424058553 | -1.3570941871 | -2.2967103323 |
| H | 1.0 | -0.5509903105 | 2.4243112404 | -1.2168957788 |
| H | 1.0 | -1.5890695518 | 1.8587828225 | -2.4945819931 |
| C | 6.0 | 0.2371257421 | 0.6664805847 | -2.2430088198 |
| H | 1.0 | 0.2424522029 | 0.6247750533 | -3.3262244593 |
| H | 1.0 | 1.1897615633 | 1.0888786772 | -1.9442104102 |

| | |
|---|---|
| Energy | -745.4943903 Hartree |
| ZPE | 0.208434 Hartree/Molecule |
| Imaginary Frequency | -1646.97 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 2.2714839254 | -.1946830576 | .7047353164 |
| H | 1.0 | 2.9203623495 | -.1081470595 | 1.5724987778 |
| H | 1.0 | 2.7545582327 | .2574900790 | -.1600638249 |
| C | 6.0 | -.7603710572 | -.5399090539 | -.3785627779 |
| C | 6.0 | -1.6888623721 | .6170975318 | -.6847247101 |
| H | 1.0 | 2.0697119012 | -1.2466460048 | .5102059701 |
| C | 6.0 | .0720270624 | -.7320947695 | -1.6228759819 |
| C | 6.0 | -1.1054526616 | -1.5416581401 | .5410049944 |
| S | 16.0 | .7245838310 | .6632232841 | 1.0422129776 |
| H | 1.0 | -.6635582074 | -2.5230001425 | .4034089762 |
| H | 1.0 | -2.1287073608 | -1.5547516178 | .9023153796 |
| H | 1.0 | -.5083876961 | -1.0100889577 | 1.6470722824 |
| O | 8.0 | .1483190449 | -.1782231388 | 2.2586029575 |
| H | 1.0 | -2.5894833589 | .2111726219 | -1.1570247621 |
| H | 1.0 | -2.0146861535 | 1.1434943865 | .2143056166 |
| C | 6.0 | -.9213880144 | 1.5175491717 | -1.6749273165 |
| H | 1.0 | .9976122643 | -1.2873908424 | -1.4654426540 |
| H | 1.0 | -.5277908719 | -1.3168502512 | -2.3296651278 |
| H | 1.0 | -.5827656837 | 2.4323335650 | -1.1895041472 |
| H | 1.0 | -1.5635365461 | 1.8188461803 | -2.5022603367 |
| C | 6.0 | .2867181906 | .6843881847 | -2.1753685139 |
| H | 1.0 | .3672086009 | .6862397975 | -3.2624451700 |
| H | 1.0 | 1.2195187813 | 1.1033434328 | -1.7950156256 |

| | |
|---|---|
| Energy | -746.8407104 Hartree |
| ZPE | 0.201374 Hartree/Molecule |
| Imaginary Frequency | -1104.17 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -747.3071786 Hartree |

**Methylenecyclopentane**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.7379465404 | 1.3306590377 | 1.5445523260 |
| C | 6.0 | 1.2297308048 | -0.1143819355 | 0.0103611469 |
| C | 6.0 | -0.7247207144 | -0.2509156139 | 1.4139600162 |
| C | 6.0 | 0.0000197499 | -0.0000244915 | -0.8788171263 |
| C | 6.0 | -1.2296944091 | 0.1144339372 | 0.0104232325 |
| H | 1.0 | -2.0469221740 | -0.5125242740 | -0.3293378845 |
| H | 1.0 | -1.5873161589 | 1.1421388858 | 0.0026843983 |
| H | 1.0 | 2.0468934382 | 0.5125188860 | -0.3293142244 |
| H | 1.0 | -0.9140170115 | 0.0674418258 | -2.7624840217 |
| C | 6.0 | 0.0000098255 | 0.0000047450 | -2.1969281118 |
| H | 1.0 | -0.7379293580 | -1.3306303243 | 1.5445158900 |
| C | 6.0 | 0.7246756271 | 0.2509015403 | 1.4139286102 |
| H | 1.0 | 0.9140044384 | -0.0674778383 | -2.7624691288 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.5872973230 | -1.1421099253 | 0.0026779602 |
| H | 1.0 | -1.3263228734 | 0.1806192553 | 2.2066172063 |
| H | 1.0 | 1.3263449522 | -0.1806537104 | 2.2066456258 |

Energy -233.0277825 Hartree
ZPE 0.154769 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.7113649879 | 1.3489873484 | 1.5180832513 |
| C | 6.0 | 1.2275396088 | -0.1222226076 | 0.0164503532 |
| C | 6.0 | -0.7196034277 | -0.2615273923 | 1.4115823100 |
| C | 6.0 | 0.0000102921 | 0.0000001587 | -0.8689076484 |
| C | 6.0 | -1.2275470409 | 0.1222285060 | 0.0164454284 |
| H | 1.0 | -2.0574771127 | -0.4940527476 | -0.3309608355 |
| H | 1.0 | -1.5744062256 | 1.1597915149 | 0.0245206012 |
| H | 1.0 | 2.0574825314 | 0.4940665695 | -0.3309539814 |
| H | 1.0 | -0.9191971519 | 0.0758135955 | -2.7718725411 |
| C | 6.0 | -0.0000353604 | 0.0000034015 | -2.2064191765 |
| H | 1.0 | -0.7113652656 | -1.3489911580 | 1.5180753527 |
| C | 6.0 | 0.7196023223 | 0.2615291086 | 1.4115762756 |
| H | 1.0 | 0.9192219897 | -0.0758331557 | -2.7718889381 |
| H | 1.0 | 1.5744084163 | -1.1597852933 | 0.0245123221 |
| H | 1.0 | -1.3284745819 | 0.1465963116 | 2.2183842409 |
| H | 1.0 | 1.3284760184 | -0.1466041606 | 2.2183889004 |

Energy -233.8651104 Hartree
ZPE 0.148909 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -234.0967281 Hartree

**Methyl 1-Methylcyclohexyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.0610458055 | -.2437815001 | -.5586302159 |
| C | 6.0 | .9117224753 | -.4556041925 | 2.5635758223 |
| H | 1.0 | 1.0844950329 | -1.5201102890 | 2.4916057725 |
| C | 6.0 | .0572745753 | -.4284968832 | -.1337147250 |
| H | 1.0 | 1.3397411888 | 1.3195541493 | .1021581182 |
| H | 1.0 | .6473963170 | -.2143424893 | 3.5849044997 |
| H | 1.0 | 1.7936397542 | .1027621100 | 2.2799815353 |
| C | 6.0 | .2932501883 | -1.9372656270 | -.2298970206 |
| S | 16.0 | -.5047663511 | .0157986365 | 1.5633478280 |
| H | 1.0 | 1.1291208169 | -2.2622737175 | .3790683085 |
| H | 1.0 | .5166781073 | -2.2071671532 | -1.2574532561 |
| H | 1.0 | -.5916811660 | -2.4764831311 | .0838712528 |
| O | 8.0 | -1.5870951781 | -.9442543023 | 1.9240363079 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.3221892552 | .3951428270 | -.4738737356 |
| C | 6.0 | -1.1230619924 | -.0277158811 | -1.0579789604 |
| C | 6.0 | -1.0474055264 | 1.4344325418 | -1.4971175049 |
| H | 1.0 | -1.9377268373 | 1.6972883716 | -2.0592808466 |
| C | 6.0 | .2135989305 | 1.6996511618 | -2.3428548262 |
| H | 1.0 | .5232937662 | 2.7331714261 | -2.2149983798 |
| H | 1.0 | -1.0967176970 | -.6653686615 | -1.9375911906 |
| H | 1.0 | 2.2101171555 | -.1619816815 | -.1927560156 |
| C | 6.0 | 1.3701466688 | .7582480930 | -1.9600234401 |
| H | 1.0 | 2.3240535609 | 1.2202748201 | -2.1949064076 |
| H | 1.0 | -1.0471983907 | 2.0731317563 | -.6180860116 |
| H | 1.0 | 1.3222830013 | -.1521910938 | -2.5515677484 |
| H | 1.0 | -.0127592827 | 1.5766202567 | -3.3981412120 |

Energy -784.6009283 Hartree
ZPE 0.246863 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.0465177890 | -0.2963417191 | -0.5882367482 |
| C | 6.0 | 0.9038579456 | -0.4503053309 | 2.5149666497 |
| H | 1.0 | 1.0511327709 | -1.5247719694 | 2.4405993824 |
| C | 6.0 | 0.0652933649 | -0.4276729612 | -0.1464732598 |
| H | 1.0 | 1.3112686064 | 1.3429437982 | 0.1068005515 |
| H | 1.0 | 0.6729675917 | -0.1956637638 | 3.5467369127 |
| H | 1.0 | 1.7903498131 | 0.0924114804 | 2.1955617753 |
| C | 6.0 | 0.3019588716 | -1.9290311749 | -0.2093324553 |
| S | 16.0 | -0.5424724126 | 0.0351702826 | 1.5422321973 |
| H | 1.0 | 1.1681375283 | -2.2348191704 | 0.3763986101 |
| H | 1.0 | 0.4751614216 | -2.2319482126 | -1.2425542512 |
| H | 1.0 | -0.5788511067 | -2.4505785453 | 0.1664205922 |
| O | 8.0 | -1.6455555072 | -0.9441971952 | 1.8987949189 |
| C | 6.0 | 1.3179454018 | 0.4062599273 | -0.4639223803 |
| C | 6.0 | -1.1034837466 | -0.0416600917 | -1.0774458640 |
| C | 6.0 | -1.0337990130 | 1.4303693483 | -1.4680471184 |
| H | 1.0 | -1.9358094883 | 1.7300101398 | -2.0033322162 |
| C | 6.0 | 0.2143830581 | 1.6968705944 | -2.3268400845 |
| H | 1.0 | 0.5312130219 | 2.7344206607 | -2.2023556823 |
| H | 1.0 | -1.0475966176 | -0.6591725525 | -1.9781835050 |
| H | 1.0 | 2.2127669235 | -0.1412444135 | -0.1605866641 |
| C | 6.0 | 1.3676802761 | 0.7521133584 | -1.9512085755 |
| H | 1.0 | 2.3287563678 | 1.2029032493 | -2.2043442653 |
| H | 1.0 | -1.0021050038 | 2.0358547671 | -0.5591984197 |
| H | 1.0 | 1.3005554872 | -0.1726523506 | -2.5287173042 |
| H | 1.0 | -0.0276951984 | 1.5697713918 | -3.3840548477 |

Energy -786.0768858 Hartree

| | |
|---|---|
| ZPE | 0.237797 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -786.5875472 Hartree |

**Transition State for Methyl 1-Methylcyclohexyl Sulfoxide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.9879671142 | -2.2134392164 | 1.4597628509 |
| H | 1.0 | -1.2844772474 | -2.6304616148 | 2.4132150438 |
| H | 1.0 | -.3973561554 | -2.9439000845 | .9184775109 |
| C | 6.0 | -.3312372028 | .6079536566 | -.2376016382 |
| C | 6.0 | 1.0291256320 | 1.2914244620 | -.2784679004 |
| H | 1.0 | -1.8745485087 | -1.9625435109 | .8907823520 |
| C | 6.0 | -.5386628804 | -.4261169248 | -1.3324691667 |
| C | 6.0 | -1.4239364960 | 1.3315290141 | .3077529039 |
| S | 16.0 | .0164611723 | -.7518309579 | 1.7570656972 |
| H | 1.0 | -2.3983378150 | 1.1025144726 | -.0997538024 |
| H | 1.0 | -1.2562257765 | 2.3900669543 | .4534239147 |
| H | 1.0 | -1.3983701234 | .8876482305 | 1.5377769322 |
| O | 8.0 | -.9507428013 | .1896568322 | 2.5265556297 |
| H | 1.0 | .8846012141 | 2.2414511312 | -.7912628799 |
| H | 1.0 | 1.3591048235 | 1.5392921949 | .7235717013 |
| C | 6.0 | 2.0679429003 | .4670320738 | -1.0344243657 |
| H | 1.0 | -.0638878601 | -1.3693644566 | -1.0895955380 |
| H | 1.0 | -1.5963783708 | -.6203615097 | -1.4650357608 |
| H | 1.0 | 3.0280809635 | .9721218232 | -1.0152055613 |
| H | 1.0 | 1.9828333080 | 1.0256920395 | -3.1259277632 |
| C | 6.0 | .0937501933 | .1061141603 | -2.6277398521 |
| H | 1.0 | -.1639136518 | -.5482880200 | -3.4542273239 |
| C | 6.0 | 1.6269625535 | .2194612222 | -2.4913511740 |
| H | 1.0 | 2.2119684390 | -.4794245395 | -.5211604982 |
| H | 1.0 | -.3372985551 | 1.0762326205 | -2.8596245940 |
| H | 1.0 | 2.0975584593 | -.6883360527 | -2.8571607178 |

| | |
|---|---|
| Energy | -784.5302657 Hartree |
| ZPE | 0.239942 Hartree/Molecule |
| Imaginary Frequency | -1664.24 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.9502617447 | -2.1423504210 | 1.3739885611 |
| H | 1.0 | -1.3098274947 | -2.5437461483 | 2.3179550464 |
| H | 1.0 | -0.3590978647 | -2.8975125929 | 0.8582092796 |
| C | 6.0 | -0.3385791856 | 0.5787939230 | -0.2134980343 |
| C | 6.0 | 1.0053347032 | 1.2945918681 | -0.2828989992 |
| H | 1.0 | -1.7962240056 | -1.8501367815 | 0.7551387555 |
| C | 6.0 | -0.5364451605 | -0.4495268996 | -1.3113525197 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -1.4341566853 | 1.3022909575 | 0.2969595171 |
| S | 16.0 | 0.0921134311 | -0.7128339474 | 1.7135799857 |
| H | 1.0 | -2.4247907863 | 1.0293615353 | -0.0513220301 |
| H | 1.0 | -1.2963208648 | 2.3648033555 | 0.4719077397 |
| H | 1.0 | -1.3728894955 | 0.8770844781 | 1.5900502470 |
| O | 8.0 | -0.8936604995 | 0.2350972616 | 2.5171328304 |
| H | 1.0 | 0.8691997625 | 2.2329224463 | -0.8320678024 |
| H | 1.0 | 1.3403958216 | 1.5771341685 | 0.7184039133 |
| C | 6.0 | 2.0426849607 | 0.4430119697 | -1.0047666695 |
| H | 1.0 | -0.0474730689 | -1.4019960644 | -1.0862205588 |
| H | 1.0 | -1.5998547191 | -0.6589441348 | -1.4449773673 |
| H | 1.0 | 3.0246210730 | 0.9177553399 | -0.9738607101 |
| H | 1.0 | 1.9876510071 | 0.9985702509 | -3.0986668225 |
| C | 6.0 | 0.0834139727 | 0.1005796184 | -2.6002968616 |
| H | 1.0 | -0.1839676657 | -0.5278855421 | -3.4518646437 |
| C | 6.0 | 1.6141151068 | 0.1941387291 | -2.4616288449 |
| H | 1.0 | 2.1441746568 | -0.5078058536 | -0.4754850271 |
| H | 1.0 | -0.3409227724 | 1.0880724765 | -2.7941538113 |
| H | 1.0 | 2.0758166174 | -0.7273459927 | -2.8228891732 |

| | |
|---|---|
| Energy | -786.0248423 Hartree |
| ZPE | 0.231356 Hartree/Molecule |
| Imaginary Frequency | -1106.09 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -786.5304520 Hartree |

**Methylenecyclohexane**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.1871504537 | 1.4802549622 | 0.8297477933 |
| C | 6.0 | 1.2363324810 | -0.3263249009 | -0.3198015545 |
| C | 6.0 | -1.2155865485 | -0.4104994226 | 1.0222176246 |
| C | 6.0 | -0.0000095357 | -0.0000002318 | -1.1381082657 |
| C | 6.0 | -1.2363365758 | 0.3262744054 | -0.3198018211 |
| H | 1.0 | -2.1319823219 | 0.0819527169 | -0.8813334091 |
| H | 1.0 | -1.2687084472 | 1.3996099007 | -0.1339046328 |
| H | 1.0 | 2.1319834370 | -0.0819473446 | -0.8813355279 |
| H | 1.0 | -0.8925675800 | 0.2073261436 | -3.0241001283 |
| C | 6.0 | 0.0000117139 | -0.0000011649 | -2.4582099253 |
| H | 1.0 | -1.1871478973 | -1.4802421635 | 0.8297511363 |
| C | 6.0 | 1.2155812839 | 0.4104997103 | 1.0222211157 |
| H | 1.0 | 0.8925568669 | -0.2073097411 | -3.0240934673 |
| H | 1.0 | 1.2687243107 | -1.3995992681 | -0.1338965695 |
| H | 1.0 | -2.1353991648 | -0.2237671538 | 1.5680976988 |
| H | 1.0 | 2.1353959790 | 0.2237688610 | 1.5680961024 |
| H | 1.0 | -0.2703402670 | 0.8261214502 | 2.5304115394 |
| C | 6.0 | 0.0000025247 | -0.0000021776 | 1.8785630442 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.2703392876 | -0.8261145815 | 2.5304033238 |

Energy -272.0644345 Hartree
ZPE 0.186193 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.1516481345 | 1.4898221792 | 0.7956222508 |
| C | 6.0 | 1.2274593621 | -0.3417454029 | -0.3094603320 |
| C | 6.0 | -1.2059357128 | -0.4210219961 | 1.0152878079 |
| C | 6.0 | 0.0000036321 | -0.0000011319 | -1.1247213472 |
| C | 6.0 | -1.2274659487 | 0.3417350062 | -0.3094545860 |
| H | 1.0 | -2.1320869993 | 0.1220766547 | -0.8794313819 |
| H | 1.0 | -1.2428340352 | 1.4167549708 | -0.0986685704 |
| H | 1.0 | 2.1320825870 | -0.1220742276 | -0.8794337877 |
| H | 1.0 | -0.8953711503 | 0.2237770783 | -3.0289922109 |
| C | 6.0 | -0.0000039657 | -0.0000017099 | -2.4641227732 |
| H | 1.0 | -1.1516362348 | -1.4898298026 | 0.7956213108 |
| C | 6.0 | 1.2059230409 | 0.4210458578 | 1.0152892621 |
| H | 1.0 | 0.8953747641 | -0.2237735750 | -3.0289925197 |
| H | 1.0 | 1.2428384288 | -1.4167554919 | -0.0986637750 |
| H | 1.0 | -2.1348288066 | -0.2656237724 | 1.5664148599 |
| H | 1.0 | 2.1348287618 | 0.2656160489 | 1.5664195663 |
| H | 1.0 | -0.2826520963 | 0.8275839269 | 2.5287528936 |
| C | 6.0 | 0.0000080438 | -0.0000132981 | 1.8747166222 |
| H | 1.0 | 0.2826481948 | -0.8275713124 | 2.5287407874 |

Energy -273.0482059 Hartree
ZPE 0.179244 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -273.3193639 Hartree

**Methyl methanesulfinate**

Lowest energy conformer

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.1453509052 | 2.1600105770 | -1.2221617443 |
| C | 6.0 | 0.8405657292 | 1.7004151952 | -0.2908703795 |
| H | 1.0 | 1.7051244390 | 1.3265731485 | 0.2411544437 |
| S | 16.0 | -0.2049507808 | 0.3144528158 | -0.6933147977 |
| H | 1.0 | 0.2895414300 | 2.4058183447 | 0.3163226281 |
| O | 8.0 | 0.6406442857 | -0.6700159335 | -1.3614165670 |
| O | 8.0 | -0.3879161317 | -0.1072489037 | 0.8691229052 |
| C | 6.0 | -1.1670019250 | -1.2695396705 | 1.0953289761 |
| H | 1.0 | -0.6841480047 | -2.1389501894 | 0.6694022771 |
| H | 1.0 | -2.1602794989 | -1.1561111605 | 0.6726122635 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.2416245201 | -1.3795260876 | 2.166781735 7 |

Energy -626.3959143 Hartree
ZPE 0.091028 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.1480496681 | 2.1713345351 | -1.2193909851 |
| C | 6.0 | .8332304427 | 1.6991613840 | -.2920283211 |
| H | 1.0 | 1.6945472141 | 1.3146518813 | .2484492212 |
| S | 16.0 | -.2046430412 | .3002918941 | -.7228335719 |
| H | 1.0 | .2694659331 | 2.3950503904 | .3230265966 |
| O | 8.0 | .6694292707 | -.6877606199 | -1.4163998713 |
| O | 8.0 | -.3660033410 | -.0827864615 | .9197290370 |
| C | 6.0 | -1.1689490041 | -1.2628809472 | 1.1057617938 |
| H | 1.0 | -.6850556229 | -2.1327084935 | .6637659944 |
| H | 1.0 | -2.1629945341 | -1.1355075084 | .6729217903 |
| H | 1.0 | -1.2517710574 | -1.3929679185 | 2.1799600570 |

Energy -627.1918608 Hartree
ZPE 0.087207 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -627.5647770 Hartree

Higher Energy Conformer

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9944162568 | -.0559119513 | -1.5859343060 |
| C | 6.0 | -1.6578646579 | .0893794332 | -.5670342638 |
| H | 1.0 | -1.6393086290 | 1.1489954224 | -.3488835924 |
| S | 16.0 | -.0013025475 | -.5847091124 | -.4601327479 |
| H | 1.0 | -2.3089695487 | -.4382919156 | .1177981098 |
| O | 8.0 | .8379516341 | .3435151603 | -1.2171424210 |
| O | 8.0 | .2550620500 | -.3557298606 | 1.1228218105 |
| C | 6.0 | .5807948479 | .9438318676 | 1.6001698733 |
| H | 1.0 | -.3055489703 | 1.5643671463 | 1.6623512750 |
| H | 1.0 | 1.3139628573 | 1.4108973769 | .9597357943 |
| H | 1.0 | .9865503075 | .7987566599 | 2.5901059910 |

Energy -626.3956315 Hartree
ZPE 0.091030 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9867293959 | -0.0063968485 | -1.5685750479 |
| C | 6.0 | -1.6137736378 | 0.1249952727 | -0.5552369264 |
| H | 1.0 | -1.5215408638 | 1.1881973041 | -0.3461745793 |

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.0193120454 | -0.6382962924 | -0.4753691542 |
| H | 1.0 | -2.2764391831 | -0.3595169797 | 0.1575997633 |
| O | 8.0 | 0.9074680363 | 0.2730217055 | -1.2541350913 |
| O | 8.0 | 0.2587359773 | -0.4243000885 | 1.1784062040 |
| C | 6.0 | 0.5150738126 | 0.9323510937 | 1.5952114624 |
| H | 1.0 | -0.4185621795 | 1.4630312681 | 1.7813981629 |
| H | 1.0 | 1.1017704279 | 1.4582900728 | 0.8431255523 |
| H | 1.0 | 1.0815960472 | 0.8537237189 | 2.5176051770 |

| | |
|---|---|
| Energy | -627.1910771 Hartree |
| ZPE | 0.087323 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -627.5629927 Hartree |

**Transition State for methyl methanesulfinate**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9372129717 | .1245361621 | -1.7972393586 |
| C | 6.0 | -1.6698667738 | -.0393169615 | -.7614979213 |
| H | 1.0 | -1.7490363692 | .8822959644 | -.2023992719 |
| S | 16.0 | .0075394004 | -.6517221956 | -.6450052105 |
| H | 1.0 | -2.3210511915 | -.7865459115 | -.3246787446 |
| O | 8.0 | .8802264363 | .5546467716 | -.9372126378 |
| O | 8.0 | .1069898985 | -.2242200739 | 1.4390883014 |
| C | 6.0 | .8380266022 | .8292017379 | 1.5116477176 |
| H | 1.0 | .3287750461 | 1.7602425259 | 1.7484933756 |
| H | 1.0 | 1.1141604505 | 1.0182217808 | .2071947836 |
| H | 1.0 | 1.8296826722 | .7043008999 | 1.9376222663 |

| | |
|---|---|
| Energy | -626.2936981 Hartree |
| ZPE | 0.084509 Hartree/Molecule |
| Imaginary Frequency | -2053.14 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.8503182588 | .3928600202 | -1.7264985084 |
| C | 6.0 | -1.6798548850 | -.0569906625 | -.7518834947 |
| H | 1.0 | -1.7950623873 | .6717334159 | .0451072366 |
| S | 16.0 | -.0298156597 | -.7537190783 | -.6629070390 |
| H | 1.0 | -2.3827003941 | -.8740671398 | -.5939887142 |
| O | 8.0 | .9070255583 | .4920538507 | -.9117224708 |
| O | 8.0 | .0774341669 | -.1843008214 | 1.5457754548 |
| C | 6.0 | .8426086013 | .8773938879 | 1.5085579999 |
| H | 1.0 | .3692372383 | 1.8598679057 | 1.6288727440 |
| H | 1.0 | 1.1101488245 | .9524865504 | .1852707708 |
| H | 1.0 | 1.8595303956 | .7943227713 | 1.9094293207 |

| | |
|---|---|
| Energy | -627.1433377 Hartree |
| ZPE | 0.080205 Hartree/Molecule |
| Imaginary Frequency | -973.90 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -627.5056343 Hartree |

**Formaldehyde**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -.0170616365 | .0000000000 | .0010581247 |
| C | 6.0 | .0237038681 | .0000000000 | 1.0936862954 |
| O | 8.0 | 1.0494688444 | .0000000000 | 1.6859111643 |
| H | 1.0 | -.9429215180 | .0000000000 | 1.6046949096 |

| | |
|---|---|
| Energy | -113.8697432 Hartree |
| ZPE | 0.028981 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -.0246764161 | .0000000000 | -.0089607096 |
| C | 6.0 | .0181853873 | .0000000000 | 1.0904990233 |
| O | 8.0 | 1.0750868233 | .0000000000 | 1.7007018805 |
| H | 1.0 | -.9554062365 | .0000000000 | 1.6031102997 |

| | |
|---|---|
| Energy | -114.1834986 Hartree |
| ZPE | 0.027468 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -114.3145654 Hartree |

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -.0157679000 | .0000000000 | -.0107378020 |
| C | 6.0 | .0169985806 | .0000000000 | 1.0898089815 |
| O | 8.0 | 1.0644530336 | .0000000000 | 1.6945630706 |
| H | 1.0 | -.9524941562 | .0000000000 | 1.6117162438 |

| | |
|---|---|
| Energy | -114.3147902 Hartree |
| ZPE | 0.026930 Hartree/Molecule |

**Methanesulfinylmethanol**

Lowest Energy Conformer-Hydrogen bonded

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -.8024219700 | -.0854967476 | .3708616746 |
| C | 6.0 | .2445717708 | .6028320182 | 1.6545079805 |
| H | 1.0 | 1.1754844079 | .9380728511 | 1.2185917983 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .4227153697 | -.1442393011 | 2.4190901878 |
| H | 1.0 | -.2857206620 | 1.4432875985 | 2.0818115647 |
| O | 8.0 | -.9615195017 | .9838248117 | -.6646661686 |
| C | 6.0 | .4183119281 | -1.1801124517 | -.4108132915 |
| O | 8.0 | 1.3903581467 | -.4165742026 | -1.0176316312 |
| H | 1.0 | -.1399618170 | -1.7844342596 | -1.1206007352 |
| H | 1.0 | .8704768568 | -1.8250146444 | .3314499950 |
| H | 1.0 | .9525301805 | .2895026424 | -1.4811628369 |

Energy -626.4022632 Hartree
ZPE 0.092221 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -0.8254837043 | -0.0680267728 | 0.3481029737 |
| C | 6.0 | 0.2428983695 | 0.5748904006 | 1.6518031545 |
| H | 1.0 | 1.2086949444 | 0.8167757084 | 1.2146989243 |
| H | 1.0 | 0.3429183932 | -0.1667293172 | 2.4428926317 |
| H | 1.0 | -0.2288782622 | 1.4726905252 | 2.0419169761 |
| O | 8.0 | -0.8944539630 | 1.0122571018 | -0.7296077018 |
| C | 6.0 | 0.4385426789 | -1.1855151680 | -0.3988198539 |
| O | 8.0 | 1.3615395620 | -0.3711347957 | -1.0542946433 |
| H | 1.0 | -0.1119843753 | -1.8453150825 | -1.0768908762 |
| H | 1.0 | 0.9373951019 | -1.7711610565 | 0.3721524180 |
| H | 1.0 | 0.8136359645 | 0.3529167717 | -1.4305154657 |

Energy -627.1931811 Hartree
ZPE 0.087911 Hartree/Molecule

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -0.8194539994 | -0.0676494821 | 0.3537271114 |
| C | 6.0 | 0.2472671636 | 0.5881654066 | 1.6355486414 |
| H | 1.0 | 1.1821211620 | 0.9091175700 | 1.1807977203 |
| H | 1.0 | 0.4134359493 | -0.1811960271 | 2.3892046005 |
| H | 1.0 | -0.2741304789 | 1.4344112743 | 2.0760101660 |
| O | 8.0 | -0.9252774424 | 1.0044292477 | -0.6921590253 |
| C | 6.0 | 0.4239514497 | -1.1834154189 | -0.3921857608 |
| O | 8.0 | 1.3890654818 | -0.4023415938 | -1.0217804763 |
| H | 1.0 | -0.1351470547 | -1.8126964013 | -1.0906864490 |
| H | 1.0 | 0.8869475623 | -1.7968021397 | 0.3797845316 |
| H | 1.0 | 0.8960449164 | 0.3296258792 | -1.4368225224 |

Energy -627.5674492 Hartree
ZPE 0.086091 Hartree/Molecule

Higher Energy Conformer-Hydroxyl rotated 60 degrees

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .6534063930 | .1319984921 | .0946764338 |
| C | 6.0 | .3902333465 | .2053913214 | 1.8702323774 |
| H | 1.0 | 1.3622665408 | .1148734534 | 2.3357938777 |
| H | 1.0 | -.2309628579 | -.6226408111 | 2.1903593969 |
| H | 1.0 | -.0576159650 | 1.1518151469 | 2.1483328659 |
| O | 8.0 | 1.2161560084 | -1.2079879195 | -.1986441581 |
| C | 6.0 | -1.0982022259 | .1154307944 | -.3788537012 |
| O | 8.0 | -1.2433792018 | .2382485908 | -1.7483212690 |
| H | 1.0 | -1.6036584858 | .9083168048 | .1683190197 |
| H | 1.0 | -1.5000156996 | -.8461207999 | -.0891515879 |
| H | 1.0 | -.9921045026 | 1.1011959807 | -2.0360632892 |

Energy -626.3919295 Hartree
ZPE 0.091433 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .6821089917 | .1283115449 | .0797504195 |
| C | 6.0 | .3782948915 | .2111276082 | 1.8629358452 |
| H | 1.0 | 1.3435935815 | .1052402077 | 2.3506631688 |
| H | 1.0 | -.2671032296 | -.6112812490 | 2.1684637361 |
| H | 1.0 | -.0648840197 | 1.1691768915 | 2.1290477521 |
| O | 8.0 | 1.2607581963 | -1.2314060800 | -.2235022474 |
| C | 6.0 | -1.0942003997 | .1163706757 | -.3646287415 |
| O | 8.0 | -1.2669969346 | .2275308748 | -1.7545654165 |
| H | 1.0 | -1.5894849572 | .9156888418 | .1985279448 |
| H | 1.0 | -1.4901449173 | -.8550079705 | -.0685819751 |
| H | 1.0 | -.9958178527 | 1.1147697090 | -2.0214305199 |

Energy -627.1811455 Hartree
ZPE 0.087139 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -627.5577530 Hartree

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.6794786888 | 0.1657710791 | 0.0901100442 |
| C | 6.0 | 0.3711913930 | 0.1871466858 | 1.8613827701 |
| H | 1.0 | 1.3413462516 | 0.0927825865 | 2.3428455209 |
| H | 1.0 | -0.2542018717 | -0.6650237900 | 2.1258560180 |
| H | 1.0 | -0.0951260913 | 1.1280503400 | 2.1507003410 |
| O | 8.0 | 1.2420749920 | -1.1687072438 | -0.2415693878 |
| C | 6.0 | -1.0880230198 | 0.1474733389 | -0.3488931750 |
| O | 8.0 | -1.2692680888 | 0.1841433638 | -1.7355164604 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.5672071152 | 0.9832893201 | 0.1726569435 |
| H | 1.0 | -1.4847906162 | -0.8041322784 | 0.0060736362 |
| H | 1.0 | -0.9793511722 | 1.0397276521 | -2.0669662848 |

Energy -627.5586070 Hartree
ZPE 0.085498 Hartree/Molecule

**Transition State for Methanesulfinylmethanol**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -.8251701852 | -.0562798018 | .3872618778 |
| C | 6.0 | .1177812679 | .6188239484 | 1.7547781698 |
| H | 1.0 | 1.1265758996 | .8224175819 | 1.4205443593 |
| H | 1.0 | .1219898204 | -.1035964954 | 2.5627467028 |
| H | 1.0 | -.3532472198 | 1.5339223976 | 2.0864893040 |
| O | 8.0 | -.6059489963 | .9918074331 | -.7457053774 |
| C | 6.0 | .6259558966 | -1.2471111286 | -.4512405422 |
| O | 8.0 | 1.1561338122 | -.4063573891 | -1.2720082021 |
| H | 1.0 | .0387307024 | -2.0658733291 | -.8608900112 |
| H | 1.0 | 1.2086976223 | -1.5579725743 | .4123589642 |
| H | 1.0 | .3264432800 | .5123926570 | -1.2364994449 |

Energy -626.3723753 Hartree
ZPE 0.086347 Hartree/Molecule
Imaginary Frequency -1438.33 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -.8858484624 | -.0652421433 | .4016956902 |
| C | 6.0 | .1229819344 | .6006923419 | 1.7311247591 |
| H | 1.0 | 1.1305459003 | .7466843402 | 1.3466567616 |
| H | 1.0 | .1253366760 | -.1066460226 | 2.5593727994 |
| H | 1.0 | -.2964838901 | 1.5492205226 | 2.0540291972 |
| O | 8.0 | -.6576794180 | .9916796977 | -.7612233221 |
| C | 6.0 | .6403087420 | -1.2371419241 | -.4276352163 |
| O | 8.0 | 1.2041890658 | -.3564372972 | -1.2055128105 |
| H | 1.0 | .0635915808 | -2.0517279292 | -.8847773683 |
| H | 1.0 | 1.1851298415 | -1.5615717122 | .4665974863 |
| H | 1.0 | .3058699298 | .5326634261 | -1.2224921764 |

Energy -627.1782965 Hartree
ZPE 0.082684 Hartree/Molecule
Imaginary Frequency -837.78 $cm^{-1}$

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -.8801707538 | -.0591403304 | .4037003207 |
| C | 6.0 | .1244627391 | .6053370935 | 1.7215087650 |
| H | 1.0 | 1.1354501913 | .7473676760 | 1.3415585665 |
| H | 1.0 | .1170869009 | -.1143804785 | 2.5404084523 |
| H | 1.0 | -.2978228591 | 1.5507427232 | 2.0520804941 |
| O | 8.0 | -.6499621675 | .9889713838 | -.7531817768 |
| C | 6.0 | .6641113628 | -1.2534137506 | -.4369919161 |
| O | 8.0 | 1.2275305195 | -.3966133352 | -1.2083795293 |
| H | 1.0 | .0626410329 | -2.0563123844 | -.8838711419 |
| H | 1.0 | 1.1786657799 | -1.5583368083 | .4842795153 |
| H | 1.0 | .2559491541 | .5879515107 | -1.2032759496 |

Energy -627.5447993 Hartree
ZPE 0.081535 Hartree/Molecule
Imaginary Frequency -403.45 $cm^{-1}$

**Hydrogen Bonded Formaldehyde to Methanesulfenic acid**

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| S | 16.0 | -1.0586341647 | 0.0415956505 | 0.5633061612 |
| C | 6.0 | 0.0750777401 | 0.7054984756 | 1.7749386575 |
| H | 1.0 | 1.1046234901 | 0.6063243709 | 1.4337030010 |
| H | 1.0 | -0.0655102161 | 0.1235313720 | 2.6869604543 |
| H | 1.0 | -0.1551567055 | 1.7498504439 | 1.9724916064 |
| O | 8.0 | -0.7497107690 | 1.0437540954 | -0.7095254096 |
| C | 6.0 | 1.0092051107 | -1.5316290739 | -0.7603469982 |
| O | 8.0 | 1.4770687716 | -0.5408998428 | -1.2937412767 |
| H | 1.0 | 0.2107942957 | -2.1191728000 | -1.2316636591 |
| H | 1.0 | 1.4031773352 | -1.9104654938 | 0.1929208370 |
| H | 1.0 | 0.0348090037 | 0.6965617805 | -1.1764075294 |

Energy -627.5508806 Hartree
ZPE 0.082000 Hartree/Molecule

**N,N-Dimethyl methanesulfinamide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.5541584758 | -0.4947520499 | 0.2132253833 |
| C | 6.0 | 0.4626521107 | -0.6762615397 | 1.2764123739 |
| H | 1.0 | 0.8909676337 | -1.6430792506 | 1.5017508022 |
| S | 16.0 | -1.2881448268 | -0.6639465425 | 1.6508773607 |
| H | 1.0 | 0.9556183542 | 0.1075693348 | 1.8349253876 |
| O | 8.0 | -1.8385763243 | -1.8782318784 | 1.0167321251 |
| N | 7.0 | -1.1851954867 | -0.8568892543 | 3.3218376606 |
| C | 6.0 | -2.3379085216 | -0.2915626255 | 4.0171887218 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.8583903431 | -2.1994265012 | 3.7920801094 |
| H | 1.0 | 0.0477537188 | -2.5590245993 | 3.3262475877 |
| H | 1.0 | -1.6536452169 | -2.9102957701 | 3.5897011359 |
| H | 1.0 | -0.6861573035 | -2.1493175753 | 4.8606612635 |
| H | 1.0 | -2.5377318463 | 0.7054228948 | 3.6473749829 |
| H | 1.0 | -2.1022448851 | -0.2198142345 | 5.0722044740 |
| H | 1.0 | -3.2361147385 | -0.8967029082 | 3.9031083313 |

Energy -645.5996207 Hartree
ZPE 0.134203 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .5628231622 | -.5173450396 | .2198706660 |
| C | 6.0 | .4482300114 | -.7659645802 | 1.2724349070 |
| H | 1.0 | .7404652764 | -1.8025762380 | 1.4194182762 |
| S | 16.0 | -1.3012001424 | -.5693375176 | 1.6616716694 |
| H | 1.0 | 1.0376898797 | -.0932216793 | 1.8891073742 |
| O | 8.0 | -1.9976024326 | -1.7497468403 | 1.0377971926 |
| N | 7.0 | -1.1196409333 | -.7499125016 | 3.3734761779 |
| C | 6.0 | -2.3621689175 | -.3134776594 | 4.0289261738 |
| C | 6.0 | -.7746783635 | -2.1177156830 | 3.7852574207 |
| H | 1.0 | .2368561142 | -2.3620185327 | 3.4722975024 |
| H | 1.0 | -1.4681007271 | -2.8579023384 | 3.3758142469 |
| H | 1.0 | -.8092638190 | -2.1558357533 | 4.8721347208 |
| H | 1.0 | -2.6371440034 | .6703023739 | 3.6545007341 |
| H | 1.0 | -2.1739170332 | -.2371749816 | 5.0982659265 |
| H | 1.0 | -3.1953072715 | -1.0043855289 | 3.8633547114 |

Energy -646.5323827 Hartree
ZPE 0.128915 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -646.9138583 Hartree

**Transition State for N,N-Dimethyl sulfinamide**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.6238289566 | 0.9531866051 | -2.3073478793 |
| C | 6.0 | -1.5926070293 | 0.4930351800 | -1.3286944068 |
| H | 1.0 | -1.7840638113 | 1.2274926935 | -0.5589723416 |
| S | 16.0 | 0.0134768368 | -0.2471099825 | -1.0551451792 |
| H | 1.0 | -2.3338829587 | -0.2951524840 | -1.2687833749 |
| O | 8.0 | 0.9794660963 | 0.9424255342 | -0.9694213255 |
| N | 7.0 | -0.2486694054 | -0.2476662902 | 1.1400503130 |
| C | 6.0 | 0.2292159149 | -1.5648404724 | 1.5205043427 |
| C | 6.0 | 0.5421959722 | 0.7910862276 | 1.4842946294 |
| H | 1.0 | 1.3004611833 | -1.6967957269 | 1.3841271440 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.4446751563 | 0.5723030903 | 2.0444443816 |
| H | 1.0 | 0.0106583987 | 1.6801200481 | 1.7962902833 |
| H | 1.0 | -0.2966182563 | -2.3288430066 | 0.9626882217 |
| H | 1.0 | 0.0027205840 | -1.6958578359 | 2.5745256351 |
| H | 1.0 | 0.9888594749 | 1.1417646198 | 0.2629897565 |

Energy -645.5101497 Hartree
ZPE 0.127663 Hartree/Molecule
Imaginary Frequency -1913.90 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.5793185100 | 1.1517103434 | -2.1961672660 |
| C | 6.0 | -1.6015636397 | .4987215487 | -1.3276426565 |
| H | 1.0 | -1.8354932318 | 1.0487465550 | -.4206405795 |
| S | 16.0 | -.0098003948 | -.3027908987 | -1.1241748451 |
| H | 1.0 | -2.3436524454 | -.2853683092 | -1.4729550217 |
| O | 8.0 | 1.0047819987 | .8897208165 | -.9743046355 |
| N | 7.0 | -.3120242817 | -.2429066154 | 1.1706595345 |
| C | 6.0 | .2293942055 | -1.5463716397 | 1.5582221722 |
| C | 6.0 | .5249203501 | .7881017695 | 1.4621560151 |
| H | 1.0 | 1.3118062669 | -1.6410773768 | 1.4062939481 |
| H | 1.0 | 1.4462409538 | .5878931669 | 2.0145579627 |
| H | 1.0 | .0378859809 | 1.7293822650 | 1.7077853281 |
| H | 1.0 | -.2674901872 | -2.3359109127 | .9953600058 |
| H | 1.0 | .0263906194 | -1.7036043754 | 2.6196172405 |
| H | 1.0 | .9999815152 | 1.0889018629 | .2627829973 |

Energy -646.4824036 Hartree
ZPE 0.122357 Hartree/Molecule
Imaginary Frequency -1013.43 $cm^{-1}$
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -646.8544325 Hartree

**Methyl Imine**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.2769449264 | .0000113048 | -1.1576276556 |
| C | 6.0 | .1898129844 | -.0000236866 | -1.1733001837 |
| N | 7.0 | -.5161942388 | .0000057450 | -.1458824233 |
| H | 1.0 | -.2825949968 | .0000105931 | -2.1442846020 |
| C | 6.0 | .1369800477 | .0000426479 | 1.1416770329 |
| H | 1.0 | 1.2252309228 | -.0000041205 | 1.0797227839 |
| H | 1.0 | -.1826857419 | -.8734277109 | 1.6998970527 |
| H | 1.0 | -.1826713838 | .8733852272 | 1.6998548891 |

Energy -133.0695299 Hartree

ZPE 0.073197 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.2866690949 | -.0000142146 | -1.1417073696 |
| C | 6.0 | .1929013408 | .0000206541 | -1.1770980588 |
| N | 7.0 | -.5525529248 | -.0000043501 | -.1391601769 |
| H | 1.0 | -.2709776265 | -.0000087367 | -2.1574636171 |
| C | 6.0 | .1350488171 | .0000048857 | 1.1440096276 |
| H | 1.0 | 1.2276589391 | .0000007840 | 1.0570027004 |
| H | 1.0 | -.1769579590 | -.8783826248 | 1.7072258153 |
| H | 1.0 | -.1769671616 | .8783836023 | 1.7072479730 |

Energy -133.5188112 Hartree
ZPE 0.070110 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -133.6575045 Hartree

**S-Methyl thiomethanesulfinate**

Lowest energy conformer-methyl rotated 60 degrees

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.9763664352 | 0.9634288901 | -2.0424548429 |
| C | 6.0 | 1.8161121730 | 0.5960064403 | -1.0374006548 |
| H | 1.0 | 2.1140671799 | -0.4420200241 | -0.9778363478 |
| S | 16.0 | 0.0505284335 | 0.7229964812 | -0.7272264788 |
| H | 1.0 | 2.3656950704 | 1.2012415083 | -0.3281256884 |
| O | 8.0 | -0.6085697521 | -0.2320411081 | -1.6352996792 |
| S | 16.0 | 0.1425083015 | -0.1101439823 | 1.1936009630 |
| C | 6.0 | -1.6435083890 | -0.1532816876 | 1.5171683639 |
| H | 1.0 | -1.7734553238 | -0.6820396102 | 2.4514798621 |
| H | 1.0 | -2.1416867134 | -0.6933339913 | 0.7248715694 |
| H | 1.0 | -2.0489115824 | 0.8449286727 | 1.6106093915 |

Energy -949.0534190 Hartree
ZPE 0.087301 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.9896186535 | .8964925760 | -2.0541032674 |
| C | 6.0 | 1.7963387074 | .5700885954 | -1.0351509066 |
| H | 1.0 | 2.0334726539 | -.4853065820 | -.9293202520 |
| S | 16.0 | .0271685802 | .7927100235 | -.7395055681 |
| H | 1.0 | 2.3711269738 | 1.1701639135 | -.3321757308 |
| O | 8.0 | -.6856409006 | -.2252894560 | -1.5810497649 |
| S | 16.0 | .1834479818 | .0797458919 | 1.2911081092 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -1.6020781432 | -.1465918205 | 1.4955545496 |
| H | 1.0 | -1.7469700268 | -.7844430066 | 2.3631251900 |
| H | 1.0 | -2.0018309833 | -.6501926551 | .6175222605 |
| H | 1.0 | -2.1155076639 | .7983641088 | 1.6533818385 |

Energy -949.7932806 Hartree
ZPE 0.084177 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -950.1610424 Hartree

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.9607740284 | 0.9951941827 | -2.0096849817 |
| C | 6.0 | 1.7920291389 | 0.6041103300 | -1.0083485749 |
| H | 1.0 | 2.1106948752 | -0.4349533509 | -0.9521662959 |
| S | 16.0 | 0.0135405119 | 0.6804238473 | -0.7460334935 |
| H | 1.0 | 2.2971403123 | 1.2202325066 | -0.2668117831 |
| O | 8.0 | -0.6030460378 | -0.2524032940 | -1.7131502807 |
| S | 16.0 | 0.1595027787 | -0.2154923412 | 1.1512282107 |
| C | 6.0 | -1.6102152490 | -0.1451553539 | 1.5074074668 |
| H | 1.0 | -1.7532928192 | -0.6332746497 | 2.4688605195 |
| H | 1.0 | -2.1650398958 | -0.6876917714 | 0.7456514771 |
| H | 1.0 | -1.9529418108 | 0.8847514834 | 1.5724341936 |

Energy -950.1626632 Hartree
ZPE 0.082095 Hartree/Molecule

Higher energy conformer-methyl eclipsed with oxygen

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9589526953 | .2614211278 | -1.9451526061 |
| C | 6.0 | -1.6854846240 | .2378045854 | -.8975039835 |
| H | 1.0 | -1.5983642948 | 1.2506517999 | -.5289395952 |
| S | 16.0 | -.0898753676 | -.5833179295 | -.8050547178 |
| H | 1.0 | -2.4187846037 | -.3191563070 | -.3302565279 |
| O | 8.0 | .8533125026 | .3384032202 | -1.4739176689 |
| S | 16.0 | .2590347728 | -.4980697355 | 1.2583317914 |
| C | 6.0 | .6998839292 | 1.2537845574 | 1.4461814515 |
| H | 1.0 | -.1759236419 | 1.8656885505 | 1.6090343972 |
| H | 1.0 | 1.2313253858 | 1.5723226284 | .5599771744 |
| H | 1.0 | 1.3533475767 | 1.3213511273 | 2.3049698140 |

Energy -949.0552059 Hartree
ZPE 0.087463 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9229716185 | .3056291031 | -1.9541211614 |
| C | 6.0 | -1.6628257299 | .2399757917 | -.8994489835 |
| H | 1.0 | -1.5758142176 | 1.2406290067 | -.4828142721 |
| S | 16.0 | -.0607827027 | -.5873702173 | -.8015785206 |
| H | 1.0 | -2.4070670133 | -.3386624419 | -.3576663921 |
| O | 8.0 | .9070625636 | .3790577355 | -1.4297011487 |
| S | 16.0 | .1673885636 | -.5001676453 | 1.3480209597 |
| C | 6.0 | .6647733654 | 1.2354681245 | 1.4354403849 |
| H | 1.0 | -.1674104247 | 1.8853684164 | 1.6910933468 |
| H | 1.0 | 1.0815504768 | 1.5153625748 | .4635842189 |
| H | 1.0 | 1.4456156771 | 1.3255931766 | 2.1848610971 |

| | |
|---|---|
| Energy | -949.7955127 Hartree |
| ZPE | 0.084534 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -950.1604359 Hartree |

**Transition State for S-Methyl thiomethanesulfinate**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9037491746 | .2660795415 | -2.1727599981 |
| C | 6.0 | -1.7358876188 | .0400728627 | -1.1280308802 |
| H | 1.0 | -1.8576944286 | .9295660190 | -.5267054267 |
| S | 16.0 | -.0716570937 | -.5971266869 | -.9271080045 |
| H | 1.0 | -2.4289932655 | -.7249683771 | -.8001380311 |
| O | 8.0 | .8143839562 | .6451198196 | -1.1751081314 |
| S | 16.0 | .1258353063 | -.3977472201 | 1.4582020655 |
| C | 6.0 | .9835925258 | 1.0445362691 | 1.3393060295 |
| H | 1.0 | .4598789501 | 1.9499897777 | 1.6020518418 |
| H | 1.0 | 1.0309890798 | 1.0575341841 | -.1119793802 |
| H | 1.0 | 2.0250011630 | 1.0092591106 | 1.6153855154 |

| | |
|---|---|
| Energy | -948.9953776 Hartree |
| ZPE | 0.081938 Hartree/Molecule |
| Imaginary Frequency | -1633.98 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9024261146 | .4025112094 | -2.1447381062 |
| C | 6.0 | -1.7309959137 | .0355291629 | -1.1361272420 |
| H | 1.0 | -1.8477648322 | .8360758528 | -.4109470258 |
| S | 16.0 | -.0745684083 | -.6485513757 | -1.0074756689 |
| H | 1.0 | -2.4356796485 | -.7625420695 | -.9057947332 |
| O | 8.0 | .8389626158 | .6470286318 | -1.1480978491 |
| S | 16.0 | .0984315114 | -.3792862254 | 1.5988887707 |
| C | 6.0 | .9697975935 | 1.0419555694 | 1.3467652511 |
| H | 1.0 | .4684616572 | 1.9948744926 | 1.4889880509 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.0231890785 | 1.0154846230 | -.0679700052 |
| H | 1.0 | 2.0342918609 | 1.0392354288 | 1.5596241578 |

Energy -949.7659237 Hartree
ZPE 0.078415 Hartree/Molecule
Imaginary Frequency -794.14 $cm^{-1}$
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -950.1202857 Hartree

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.8899990974 | .4133832883 | -2.1337599963 |
| C | 6.0 | -1.7206728226 | .0447198524 | -1.1246809811 |
| H | 1.0 | -1.8186688023 | .8420175559 | -.3911390570 |
| S | 16.0 | -.0841773274 | -.6606645158 | -.9974551593 |
| H | 1.0 | -2.4263818020 | -.7531744766 | -.8909459563 |
| O | 8.0 | .8442377625 | .6178901614 | -1.1650299614 |
| S | 16.0 | .1101658293 | -.3778854603 | 1.5375647829 |
| C | 6.0 | .9526349993 | 1.0493766017 | 1.4348113696 |
| H | 1.0 | .4349614057 | 2.0013972192 | 1.5103498674 |
| H | 1.0 | 1.0107981312 | .9889565895 | -.1858926197 |
| H | 1.0 | 2.0288011238 | 1.0562984844 | 1.5792933115 |

Energy -950.1213994 Hartree
ZPE 0.077940 Hartree/Molecule
Imaginary Frequency -174.18 $cm^{-1}$

**Thioformaldehyde**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .9134310266 | .0000000000 | -1.6256375461 |
| C | 6.0 | .0000000000 | .0000000000 | -1.0515038836 |
| S | 16.0 | -.0000000018 | .0000000000 | .5452727997 |
| H | 1.0 | -.9134310248 | .0000000000 | -1.6256375419 |

Energy -436.5099531 Hartree
ZPE 0.026671 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .9202789896 | .0000000000 | -1.6314702933 |
| C | 6.0 | -.0000010850 | .0000000000 | -1.0551171555 |
| S | 16.0 | .0000000700 | .0000000000 | .5605510571 |
| H | 1.0 | -.9202779746 | .0000000000 | -1.6314697804 |

Energy -436.7709637 Hartree
ZPE 0.025602 Hartree/Molecule

MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -436.8884082 Hartree

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | .9234776803 | .0000000000 | -1.6286651014 |
| C | 6.0 | .0000031756 | .0000000000 | -1.0549638675 |
| S | 16.0 | -.0000002119 | .0000000000 | .5547893863 |
| H | 1.0 | -.9234806442 | .0000000000 | -1.6286665894 |

Energy -436.8884462 Hartree
ZPE 0.024908 Hartree/Molecule

**Merged Van der Waals complex of Thioformaldehyde and Methanesulfenic acid**

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.8719359760 | 0.5112521635 | -2.1356370477 |
| C | 6.0 | -1.7278726916 | 0.0524237452 | -1.1602592432 |
| H | 1.0 | -1.8492014132 | 0.7811237183 | -0.3612068282 |
| S | 16.0 | -0.1053356562 | -0.6849434687 | -1.0573048815 |
| H | 1.0 | -2.4447743532 | -0.7579157426 | -1.0213903001 |
| O | 8.0 | 0.8436167175 | 0.6140255497 | -1.2177083356 |
| S | 16.0 | 0.1365088051 | -0.3616347493 | 1.5964013700 |
| C | 6.0 | 0.9501342162 | 1.0629668571 | 1.5511948285 |
| H | 1.0 | 0.4255673353 | 2.0149140629 | 1.5639328815 |
| H | 1.0 | 1.0084713624 | 0.9706781570 | -0.2898665997 |
| H | 1.0 | 2.0339538542 | 1.0914599127 | 1.6246831846 |

Energy -950.1215461 Hartree
ZPE 0.079126 Hartree/Molecule

**(3R,SS) 3-Methanesuflinyl-3-methyl-4,5-dihydro-2-furanone**

Lowest Energy Conformer

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 2.0854092174 | .4350468876 | .3443348594 |
| O | 8.0 | -1.0378935940 | -.2312733254 | 1.8819148873 |
| C | 6.0 | -.8118070964 | -1.5892719183 | 1.5152331412 |
| C | 6.0 | .5531117116 | -1.5901469642 | .8247005951 |
| C | 6.0 | .6769468165 | -.1540651725 | .2862676857 |
| C | 6.0 | -.2917972235 | .6089990135 | 1.1929197105 |
| S | 16.0 | .0634263424 | -.1730058394 | -1.4441157163 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.6025875590 | -1.8968330230 | .8502707894 |
| H | 1.0 | -.8323688365 | -2.1766960773 | 2.4214099666 |
| H | 1.0 | 1.3447010988 | -1.7669820318 | 1.5448535512 |
| H | 1.0 | .6223641264 | -2.3524569773 | .0587666887 |
| O | 8.0 | -.3534699915 | 1.7863370319 | 1.3016402977 |
| H | 1.0 | 2.4896979225 | .3184767825 | 1.3434858621 |
| H | 1.0 | 2.0776221939 | 1.4922685181 | .1169180541 |
| H | 1.0 | 2.7470264748 | -.0759384131 | -.3474315258 |
| O | 8.0 | -1.3397545761 | -.6647550808 | -1.3673230344 |
| C | 6.0 | -.0365519810 | 1.5742684465 | -1.8405779679 |
| H | 1.0 | -.6279492423 | 2.1036948568 | -1.1089450300 |
| H | 1.0 | -.5208485244 | 1.6147993133 | -2.8077298944 |
| H | 1.0 | .9553335202 | 1.9990460729 | -1.9166972203 |

Energy -855.0989793 Hartree
ZPE 0.171451 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 2.0912541102 | .4403537624 | .3028154363 |
| O | 8.0 | -1.0938358733 | -.2116193198 | 1.8483136054 |
| C | 6.0 | -.8315360710 | -1.5870624583 | 1.4678840442 |
| C | 6.0 | .5716221983 | -1.5749695475 | .8614232445 |
| C | 6.0 | .6948108274 | -.1578061592 | .3007937556 |
| C | 6.0 | -.2693003007 | .6291931928 | 1.1812914663 |
| S | 16.0 | .0419390161 | -.2206446374 | -1.4359145453 |
| H | 1.0 | -1.5843443930 | -1.8822550938 | .7429550122 |
| H | 1.0 | -.9094548917 | -2.1853632148 | 2.3724517977 |
| H | 1.0 | 1.3262574049 | -1.7122936553 | 1.6376427528 |
| H | 1.0 | .7061159355 | -2.3575075842 | .1138298597 |
| O | 8.0 | -.3121014929 | 1.8390318951 | 1.3006971164 |
| H | 1.0 | 2.5526671920 | .2778583912 | 1.2765454283 |
| H | 1.0 | 2.0497448746 | 1.5129384488 | .1283452850 |
| H | 1.0 | 2.7209642115 | -.0294988229 | -.4535550012 |
| O | 8.0 | -1.3881115258 | -.7116617356 | -1.3529397408 |
| C | 6.0 | -.0340554780 | 1.5468667153 | -1.7909537807 |
| H | 1.0 | -.6172062028 | 2.0649997888 | -1.0345266871 |
| H | 1.0 | -.5243627244 | 1.6205749168 | -2.7592276966 |
| H | 1.0 | .9695439832 | 1.9603772176 | -1.8579756527 |

Energy -856.6088370 Hartree
ZPE 0.163452 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -857.2206273 Hartree

Next Lowest Energy Conformer

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.6436980366 | -1.1896289911 | 1.6995770743 |
| O | 8.0 | .8198888022 | -1.3319972425 | -1.4870394375 |
| C | 6.0 | 1.9645057355 | -.7881647406 | -.8398050576 |
| C | 6.0 | 1.5142296607 | -.3680903292 | .5673092431 |
| C | 6.0 | -.0135061282 | -.4535964737 | .5133165905 |
| C | 6.0 | -.2989041267 | -1.1729691775 | -.7954474322 |
| S | 16.0 | -.8085933930 | 1.2161362481 | .4905458815 |
| H | 1.0 | 2.3205157622 | .0407920801 | -1.4365017438 |
| H | 1.0 | 2.7269545345 | -1.5533068311 | -.8274835566 |
| H | 1.0 | 1.8932090669 | -1.0597061375 | 1.3096392053 |
| H | 1.0 | 1.8529337424 | .6205130105 | .8467145301 |
| O | 8.0 | -1.3581031220 | -1.5329919411 | -1.1782510201 |
| H | 1.0 | -.2058530983 | -2.1767447249 | 1.8006412897 |
| H | 1.0 | -1.7105940103 | -1.3012047163 | 1.5558607379 |
| H | 1.0 | -.4607967682 | -.6369788412 | 2.6137761832 |
| O | 8.0 | -.0416834293 | 2.0186513661 | 1.4794007059 |
| C | 6.0 | -.3169351491 | 1.8314600811 | -1.1245661688 |
| H | 1.0 | .7608672533 | 1.8782528293 | -1.2028297196 |
| H | 1.0 | -.7108376869 | 2.8374529793 | -1.1854906870 |
| H | 1.0 | -.7471932091 | 1.2291551524 | -1.9136144182 |

Energy -855.0952500 Hartree
ZPE 0.171212 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.6792837619 | -1.1888963492 | 1.7004780999 |
| O | 8.0 | 0.8335439863 | -1.1994936099 | -1.5459170811 |
| C | 6.0 | 1.9775338015 | -0.6817539355 | -0.8235484598 |
| C | 6.0 | 1.5186700029 | -0.4147540253 | 0.6159912459 |
| C | 6.0 | 0.0040554981 | -0.4803309897 | 0.5406520669 |
| C | 6.0 | -0.2965230876 | -1.1342335311 | -0.7877869057 |
| S | 16.0 | -0.7204593191 | 1.2577615598 | 0.5406968194 |
| H | 1.0 | 2.3126799169 | 0.2175798062 | -1.3386795628 |
| H | 1.0 | 2.7626555067 | -1.4320060598 | -0.8881356736 |
| H | 1.0 | 1.8880317596 | -1.1875141555 | 1.2897485499 |
| H | 1.0 | 1.8459148249 | 0.5537730761 | 1.0025043781 |
| O | 8.0 | -1.3793942835 | -1.5198944129 | -1.1817765972 |
| H | 1.0 | -0.2664690795 | -2.1904310500 | 1.8178919413 |
| H | 1.0 | -1.7480114984 | -1.2726190807 | 1.5123887748 |
| H | 1.0 | -0.5147513017 | -0.6352639874 | 2.6249882468 |
| O | 8.0 | 0.1955554759 | 2.0750773569 | 1.4258443340 |
| C | 6.0 | -0.3469484576 | 1.7428125789 | -1.1621692816 |
| H | 1.0 | 0.7267277439 | 1.7282734590 | -1.3316237013 |
| H | 1.0 | -0.7048725525 | 2.7655366511 | -1.2580303661 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.8722487750 | 1.1034102995 | -1.8677646277 |

Energy -856.6062823 Hartree
ZPE 0.163295 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -857.2180696 Hartree

Highest Energy Conformer

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.5521987835 | -.5893989075 | 1.7620665631 |
| O | 8.0 | .7386613751 | -1.7329385465 | -1.3810529212 |
| C | 6.0 | 1.9495782156 | -1.1134346181 | -.9860107211 |
| C | 6.0 | 1.6910064274 | -.6097487173 | .4344648579 |
| C | 6.0 | .1763986830 | -.3627298397 | .4418289076 |
| C | 6.0 | -.2892668218 | -1.3828195770 | -.6071011888 |
| S | 16.0 | -.2038767427 | 1.2996538580 | -.2763249660 |
| H | 1.0 | 2.1722769547 | -.3085820187 | -1.6753923041 |
| H | 1.0 | 2.7358341288 | -1.8519184810 | -1.0426156376 |
| H | 1.0 | 1.9197147493 | -1.3853887903 | 1.1578474077 |
| H | 1.0 | 2.2956868064 | .2531548985 | .6799485330 |
| O | 8.0 | -1.3668359770 | -1.8409623774 | -.7181892065 |
| H | 1.0 | -.4975340092 | -1.6368606575 | 2.0364960379 |
| H | 1.0 | -1.5942212468 | -.3209607505 | 1.6549829193 |
| H | 1.0 | -.1086966422 | -.0096735763 | 2.5629799541 |
| O | 8.0 | -1.6757468015 | 1.4583620997 | -.2609084768 |
| C | 6.0 | .3973944182 | 2.3684712007 | 1.0383718923 |
| H | 1.0 | -.1787585718 | 2.2041392868 | 1.9376791788 |
| H | 1.0 | .2186927913 | 3.3774632061 | .6900487296 |
| H | 1.0 | 1.4549192465 | 2.2359617080 | 1.2189801408 |

Energy -855.0876184 Hartree
ZPE 0.171017 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.5292088284 | -.5419509654 | 1.7763968265 |
| O | 8.0 | .7327683687 | -1.7454903395 | -1.4002687655 |
| C | 6.0 | 1.9484608241 | -1.0759185319 | -1.0045828762 |
| C | 6.0 | 1.7099889556 | -.6249333278 | .4360400952 |
| C | 6.0 | .2068375056 | -.3763189401 | .4624447916 |
| C | 6.0 | -.2943426369 | -1.3929876832 | -.5633821712 |
| S | 16.0 | -.1753398145 | 1.2788890811 | -.3218138513 |
| H | 1.0 | 2.1180808973 | -.2331018866 | -1.6755623379 |
| H | 1.0 | 2.7621250248 | -1.7894741693 | -1.1109479104 |
| H | 1.0 | 1.9425242542 | -1.4332988593 | 1.1320940461 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 2.3219370777 | .2352131089 | .7062265735 |
| O | 8.0 | -1.4055258779 | -1.8613969580 | -.6492786220 |
| H | 1.0 | -.5373738578 | -1.5927391679 | 2.0629842273 |
| H | 1.0 | -1.5615270036 | -.2182076998 | 1.6462971115 |
| H | 1.0 | -.0599956600 | .0302094382 | 2.5744556311 |
| O | 8.0 | -1.6763182631 | 1.4136588777 | -.3712490166 |
| C | 6.0 | .3762319375 | 2.3249994385 | 1.0505792800 |
| H | 1.0 | -.3008167093 | 2.1897891687 | 1.8902862684 |
| H | 1.0 | .2995190191 | 3.3499766887 | .6944832115 |
| H | 1.0 | 1.4050029867 | 2.1148721271 | 1.3328971885 |

| | |
|---|---|
| Energy | -856.5994648 Hartree |
| ZPE | 0.163164 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -857.2116252 Hartree |

**(3R,SS) Transition State for formation of (5H) 3-methyl-2-furanone from (3R,SS) 3-methanesuflinyl-3-methyl-4,5-dihydro-2-furanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .3248747349 | 1.6041909595 | 1.6764558473 |
| O | 8.0 | -.8968275424 | .7234619144 | -1.6361133459 |
| C | 6.0 | -2.0051467318 | .2226871877 | -.8877256529 |
| C | 6.0 | -1.5202735823 | .1639827522 | .5549813507 |
| C | 6.0 | -.2386642914 | .7591092293 | .5677394105 |
| C | 6.0 | .0874382096 | 1.1367061392 | -.8503053648 |
| S | 16.0 | 1.0272452967 | -1.1597187638 | .7993210384 |
| H | 1.0 | -2.2707604278 | -.7363291229 | -1.3120164552 |
| H | 1.0 | -2.8356395231 | .9045672840 | -1.0256533558 |
| H | 1.0 | -2.2178798562 | .4085723505 | 1.3404877610 |
| H | 1.0 | -1.1217506663 | -1.1102857276 | .8399327012 |
| O | 8.0 | 1.0536734621 | 1.7006971210 | -1.2371596139 |
| H | 1.0 | -.1956498066 | 2.5578066005 | 1.6891010633 |
| H | 1.0 | 1.3783350433 | 1.7952367473 | 1.5231641163 |
| H | 1.0 | .1818247273 | 1.1285941690 | 2.6388979385 |
| O | 8.0 | -.2722101267 | -1.9686986534 | 1.0357489038 |
| C | 6.0 | 1.5095331107 | -1.5855583635 | -.8787644281 |
| H | 1.0 | .6743149821 | -1.4712058469 | -1.5562812049 |
| H | 1.0 | 1.8487202021 | -2.6126287111 | -.8894455274 |
| H | 1.0 | 2.3139460857 | -.9255213652 | -1.1769611822 |

| | |
|---|---|
| Energy | -855.0324505 Hartree |
| ZPE | 0.164594 Hartree/Molecule |
| Imaginary Frequency | -1781.89 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .3247969612 | 1.6223589743 | 1.6784816230 |
| O | 8.0 | -.8499029375 | .6222749296 | -1.6712865346 |
| C | 6.0 | -1.9766509327 | .1650051470 | -.8926371173 |
| C | 6.0 | -1.5140289458 | .1769160691 | .5531247404 |
| C | 6.0 | -.2482059863 | .7986178669 | .5661204446 |
| C | 6.0 | .1216819184 | 1.1193272142 | -.8302375706 |
| S | 16.0 | 1.0488466146 | -1.2085259000 | .8361816658 |
| H | 1.0 | -2.2528920258 | -.8186177377 | -1.2721481968 |
| H | 1.0 | -2.8054319436 | .8549878374 | -1.0604058315 |
| H | 1.0 | -2.2359847455 | .3799903962 | 1.3377329812 |
| H | 1.0 | -1.1443055381 | -1.0773669532 | .8432938031 |
| O | 8.0 | 1.1168089882 | 1.6834697306 | -1.2489604211 |
| H | 1.0 | -.1839824175 | 2.5868214847 | 1.7310414087 |
| H | 1.0 | 1.3829688376 | 1.8073690409 | 1.5022432179 |
| H | 1.0 | .2070950493 | 1.1238808177 | 2.6399914484 |
| O | 8.0 | -.3219919600 | -1.9723151387 | 1.0445628000 |
| C | 6.0 | 1.4719795595 | -1.5399170295 | -.8816361294 |
| H | 1.0 | .6291338863 | -1.2978190454 | -1.5254808688 |
| H | 1.0 | 1.7397826436 | -2.5874941918 | -.9902153227 |
| H | 1.0 | 2.3153862739 | -.9032976122 | -1.1443621404 |

| | |
|---|---|
| Energy | -856.5712297 Hartree |
| ZPE | 0.157036 Hartree/Molecule |
| Imaginary Frequency | -961.67 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -857.1772827 Hartree |

**(3R,SS) Transition State for formation of 3-methylene-4,5-dihydro-2-furanone from (3R,SS) 3-methanesuflinyl-3-methyl-4,5-dihydro-2-furanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -1.0531770734 | 1.0135127765 | -1.3483675188 |
| O | 8.0 | .7919739237 | 1.2757087691 | 1.7457328644 |
| C | 6.0 | 1.9126857724 | .9604238548 | .9361091491 |
| C | 6.0 | 1.4165509105 | 1.0753290044 | -.5069348558 |
| C | 6.0 | -.0666340008 | .8521414292 | -.3592424251 |
| C | 6.0 | -.3612268683 | 1.1795498511 | 1.0811035702 |
| S | 16.0 | -.3395980402 | -1.5075739993 | -.0595527797 |
| H | 1.0 | 2.2448442631 | -.0416865063 | 1.1813105072 |
| H | 1.0 | 2.7034200825 | 1.6558520938 | 1.1755963004 |
| H | 1.0 | 1.5616122990 | 2.0878926180 | -.8745939991 |
| H | 1.0 | 1.9204644720 | .4071399743 | -1.1904845898 |
| O | 8.0 | -1.4167699187 | 1.3496562536 | 1.5782537242 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -1.9506855485 | 1.5175261085 | -1.0238249276 |
| H | 1.0 | -1.4786549158 | -.2375257469 | -1.4150217695 |
| H | 1.0 | -.7066991339 | 1.2808449663 | -2.3352498070 |
| O | 8.0 | -1.5175027572 | -1.4525119856 | -1.0492116336 |
| C | 6.0 | .9961751711 | -2.1752196192 | -1.0589846071 |
| H | 1.0 | 1.1176835583 | -1.5984509600 | -1.9668108961 |
| H | 1.0 | .7490064267 | -3.1950320592 | -1.3219479346 |
| H | 1.0 | 1.9131441778 | -2.1682051232 | -.4815567716 |

Energy -855.0218231 Hartree
ZPE 0.164760 Hartree/Molecule
Imaginary Frequency -1763.04 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -1.0546703123 | .9957683956 | -1.3526984976 |
| O | 8.0 | .8057604864 | 1.2878448879 | 1.7560666960 |
| C | 6.0 | 1.9116442307 | .9087988840 | .9124458286 |
| C | 6.0 | 1.4259454586 | 1.0977919634 | -.5251348089 |
| C | 6.0 | -.0534414071 | .8904795552 | -.3738678478 |
| C | 6.0 | -.3707151687 | 1.2058674193 | 1.0435100324 |
| S | 16.0 | -.3422984508 | -1.5335416101 | .0049124695 |
| H | 1.0 | 2.1652127657 | -.1335015045 | 1.1219820328 |
| H | 1.0 | 2.7582501049 | 1.5373726676 | 1.1788205890 |
| H | 1.0 | 1.6130154503 | 2.1242197952 | -.8522354380 |
| H | 1.0 | 1.9266454249 | .4336731403 | -1.2289890109 |
| O | 8.0 | -1.4578501792 | 1.3741483008 | 1.5599709259 |
| H | 1.0 | -1.9770265351 | 1.4659299814 | -1.0262481397 |
| H | 1.0 | -1.4742377542 | -.2603585165 | -1.3994315513 |
| H | 1.0 | -.7444383132 | 1.2231012227 | -2.3666879000 |
| O | 8.0 | -1.5365605595 | -1.4465617849 | -1.0209720553 |
| C | 6.0 | 1.0085515317 | -2.1302553273 | -1.0277044636 |
| H | 1.0 | 1.1222841726 | -1.4856982940 | -1.8970821193 |
| H | 1.0 | .7834506770 | -3.1411204633 | -1.3581745637 |
| H | 1.0 | 1.9270911776 | -2.1345870130 | -.4421605781 |

Energy -856.5600742 Hartree
ZPE 0.157219 Hartree/Molecule
Imaginary Frequency -977.38 $cm^{-1}$
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -857.1669804 Hartree

**(3R,SR) 3-Methanesuflinyl-3-methyl-4,5-dihydro-2-furanone**

Lowest Energy Conformer

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.3383284792 | -.8319140367 | 1.5467753805 |
| O | 8.0 | .8408829764 | -1.7359697070 | -1.3642498004 |
| C | 6.0 | 1.9839598128 | -1.5215558843 | -.5445498554 |
| C | 6.0 | 1.7149901469 | -.2005061650 | .1752792194 |
| C | 6.0 | .1806008708 | -.1885841565 | .2543985882 |
| C | 6.0 | -.2042203033 | -1.0287624808 | -.9592741771 |
| S | 16.0 | -.3774516278 | 1.5472182022 | .0771000286 |
| H | 1.0 | 2.8503979428 | -1.4950416627 | -1.1879705246 |
| H | 1.0 | 2.0790345881 | -2.3575542573 | .1374188271 |
| H | 1.0 | 2.1854816345 | -.1387317267 | 1.1460892971 |
| H | 1.0 | 2.0782323244 | .6263451035 | -.4254137047 |
| O | 8.0 | -1.2641143717 | -1.0801791886 | -1.4827588771 |
| H | 1.0 | .1945163373 | -1.7552674059 | 1.7498986065 |
| H | 1.0 | -1.3926035752 | -1.0670441048 | 1.4798751274 |
| H | 1.0 | -.1704540912 | -.1502132612 | 2.3712513124 |
| C | 6.0 | -2.1512975572 | 1.3981295188 | .2873960442 |
| O | 8.0 | .1375526813 | 2.2228894798 | 1.2992677777 |
| H | 1.0 | -2.5537134108 | .7093221856 | -.4406132576 |
| H | 1.0 | -2.5527267231 | 2.3911205110 | .1304111703 |
| H | 1.0 | -2.3737180760 | 1.0864279368 | 1.2984008176 |

Energy -855.0973174 Hartree
ZPE 0.171509 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.3374151031 | -0.8132937451 | 1.5290614160 |
| O | 8.0 | 0.8468855252 | -1.7284544777 | -1.4143000739 |
| C | 6.0 | 1.9697490149 | -1.5341630385 | -0.5203594870 |
| C | 6.0 | 1.7087830377 | -0.1939845732 | 0.1583630280 |
| C | 6.0 | 0.1823009435 | -0.1835541114 | 0.2411019400 |
| C | 6.0 | -0.2175232873 | -0.9930010471 | -0.9849827892 |
| S | 16.0 | -0.3545050875 | 1.5814518178 | 0.1031536474 |
| H | 1.0 | 2.8709741858 | -1.5548676984 | -1.1276620090 |
| H | 1.0 | 1.9946645531 | -2.3642455622 | 0.1872759829 |
| H | 1.0 | 2.1873704416 | -0.0977153491 | 1.1305596527 |
| H | 1.0 | 2.0640853590 | 0.6152650427 | -0.4826069424 |
| O | 8.0 | -1.3000625719 | -1.0312102547 | -1.5357657177 |
| H | 1.0 | 0.2278510454 | -1.7141757514 | 1.7690131901 |
| H | 1.0 | -1.3880593704 | -1.0838226473 | 1.4467278314 |
| H | 1.0 | -0.2024160743 | -0.0940809055 | 2.3383008579 |
| C | 6.0 | -2.1326619008 | 1.3619752941 | 0.3041731224 |
| O | 8.0 | 0.1615242302 | 2.2335992067 | 1.3691199801 |
| H | 1.0 | -2.4934839046 | 0.6418964221 | -0.4255479070 |
| H | 1.0 | -2.5825107597 | 2.3385770518 | 0.1396419702 |
| H | 1.0 | -2.3385291771 | 1.0439332265 | 1.3234643071 |

| | |
|---|---|
| Energy | -856.6065388 Hartree |
| ZPE | 0.163650 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -857.2181934 Hartree |

Next Lowest Energy Conformer

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.8453918937 | .4297905559 | .9652697184 |
| O | 8.0 | -1.5577711451 | -.1150571443 | 1.6337821480 |
| C | 6.0 | -1.3520884434 | -1.4390952893 | 1.1511135318 |
| C | 6.0 | .1218325743 | -1.4981385655 | .7442045476 |
| C | 6.0 | .4754575205 | -.0318151350 | .4630805682 |
| C | 6.0 | -.6281779492 | .7241084072 | 1.2176302563 |
| S | 16.0 | .2402412343 | .4078609481 | -1.3067172266 |
| H | 1.0 | -2.0053761533 | -1.5993539302 | .3082164842 |
| H | 1.0 | -1.6026998426 | -2.1175235746 | 1.9532356583 |
| H | 1.0 | .7321725653 | -1.8589780513 | 1.5656217120 |
| H | 1.0 | .2661338345 | -2.1546162462 | -.1020421132 |
| O | 8.0 | -.6395175668 | 1.8858849108 | 1.4304252908 |
| H | 1.0 | 1.8798817654 | .3557884422 | 2.0460959979 |
| H | 1.0 | 2.0263135926 | 1.4651927748 | .7031286529 |
| H | 1.0 | 2.6401677031 | -.1878273727 | .5649693196 |
| C | 6.0 | 1.6573621566 | -.4147170897 | -2.0433326815 |
| O | 8.0 | -.9504079621 | -.3701853726 | -1.7451057306 |
| H | 1.0 | 2.5732108790 | .1034786931 | -1.7946589135 |
| H | 1.0 | 1.4925901938 | -.3582220946 | -3.1115153022 |
| H | 1.0 | 1.7073107497 | -1.4551009661 | -1.7511924186 |

| | |
|---|---|
| Energy | -855.0951979 Hartree |
| ZPE | 0.171333 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.8605356820 | .4267670640 | .9298370884 |
| O | 8.0 | -1.5899037715 | -.1075326549 | 1.6294616190 |
| C | 6.0 | -1.3602449022 | -1.4409110167 | 1.1077211307 |
| C | 6.0 | .1266134225 | -1.4989889849 | .7514203847 |
| C | 6.0 | .4845136264 | -.0423705009 | .4805561976 |
| C | 6.0 | -.5953556072 | .7290744933 | 1.2458966232 |
| S | 16.0 | .1843386045 | .3928521401 | -1.2988568736 |
| H | 1.0 | -1.9839200317 | -1.5700383211 | .2279949282 |
| H | 1.0 | -1.6481587413 | -2.1392197527 | 1.8899649517 |
| H | 1.0 | .7155612892 | -1.8581266812 | 1.5970673686 |
| H | 1.0 | .2975591002 | -2.1593127538 | -.0980474864 |

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -.5750489139 | 1.9145630235 | 1.5033530199 |
| H | 1.0 | 1.9181479287 | .3760417702 | 2.0166096884 |
| H | 1.0 | 2.0230321387 | 1.4652484257 | .6427016564 |
| H | 1.0 | 2.6509113072 | -.1960538510 | .5163024156 |
| C | 6.0 | 1.6481890685 | -.4038421941 | -2.0028078584 |
| O | 8.0 | -.9971275777 | -.4476574333 | -1.7377759046 |
| H | 1.0 | 2.5474728081 | .1572967631 | -1.7620172717 |
| H | 1.0 | 1.4882321429 | -.3900912716 | -3.0788219684 |
| H | 1.0 | 1.7266800269 | -1.4362243638 | -1.6683502097 |

Energy -856.6050047 Hartree
ZPE 0.163529 Hartree/Molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -857.2166840 Hartree

Highest Energy Conformer

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.5706141542 | -.8381664037 | 1.7048106130 |
| O | 8.0 | .9706168853 | -1.7499484835 | -1.0442225016 |
| C | 6.0 | 2.0133707790 | -1.5639447420 | -.1004747424 |
| C | 6.0 | 1.6773846600 | -.2549220883 | .6125241284 |
| C | 6.0 | .1479340463 | -.2042407831 | .5041112465 |
| C | 6.0 | -.1254704711 | -1.0590296570 | -.7324778040 |
| S | 16.0 | -.4234516177 | 1.5446324131 | .4114041651 |
| H | 1.0 | 2.9486106574 | -1.5368738137 | -.6399499129 |
| H | 1.0 | 2.0249727782 | -2.4100381955 | .5761520196 |
| H | 1.0 | 2.0278267872 | -.2320807498 | 1.6360047071 |
| H | 1.0 | 2.1347085415 | .5789058057 | .0888171086 |
| O | 8.0 | -1.1313931628 | -1.1448257580 | -1.3420941553 |
| H | 1.0 | -.2377067832 | -1.8617861695 | 1.8452915554 |
| H | 1.0 | -1.6382721452 | -.8317980435 | 1.5406065801 |
| H | 1.0 | -.3554820625 | -.2825408247 | 2.6109462408 |
| C | 6.0 | -.2221990186 | 1.8773664673 | -1.3424122730 |
| O | 8.0 | -1.8777728338 | 1.5866577667 | .6836983363 |
| H | 1.0 | .7962694761 | 1.6864535141 | -1.6586667155 |
| H | 1.0 | -.4462548989 | 2.9273177354 | -1.4769988929 |
| H | 1.0 | -.9242802630 | 1.2781722100 | -1.9032198033 |

Energy -855.0902047 Hartree
ZPE 0.171200 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.5770069394 | -.8379291134 | 1.7070833591 |
| O | 8.0 | 1.0012430788 | -1.6752388470 | -1.1307466393 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 2.0273294046 | -1.5216540848 | -.1256664271 |
| C | 6.0 | 1.6753101060 | -.2367340813 | .6192018600 |
| C | 6.0 | .1530559174 | -.2124853062 | .5225769159 |
| C | 6.0 | -.1381688520 | -1.0253837347 | -.7305074064 |
| S | 16.0 | -.4318763815 | 1.5577543419 | .4442715876 |
| H | 1.0 | 2.9840908116 | -1.4883674368 | -.6409491587 |
| H | 1.0 | 2.0042161109 | -2.3935039676 | .5302418094 |
| H | 1.0 | 2.0384204051 | -.2304230409 | 1.6457806920 |
| H | 1.0 | 2.1124069907 | .6205199233 | .1017671823 |
| O | 8.0 | -1.1900931753 | -1.1314241903 | -1.3230060113 |
| H | 1.0 | -.2729432760 | -1.8772519763 | 1.8344913681 |
| H | 1.0 | -1.6495542028 | -.7965343640 | 1.5285674335 |
| H | 1.0 | -.3523413605 | -.2934231448 | 2.6243869108 |
| C | 6.0 | -.1969753309 | 1.8135449552 | -1.3310556708 |
| O | 8.0 | -1.9142892206 | 1.6056526928 | .7113411467 |
| H | 1.0 | .8114944376 | 1.5349857326 | -1.6327790604 |
| H | 1.0 | -.3555637647 | 2.8727473809 | -1.5182966541 |
| H | 1.0 | -.9399575590 | 1.2244584613 | -1.8628533374 |

| | |
|---|---|
| Energy | -856.6015064 Hartree |
| ZPE | 0.163203 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -857.2133333 Hartree |

**(3R,SR) Transition State for formation of (5H) 3-methyl-2-furanone from (3R,SR) 3-methanesuflinyl-3-methyl-4,5-dihydro-2-furanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .3461660980 | 1.6991593728 | 1.2056727148 |
| O | 8.0 | -.7521218215 | .5703612046 | -2.0526876973 |
| C | 6.0 | -1.9510644293 | .2686530774 | -1.3426956725 |
| C | 6.0 | -1.5581836912 | .2870828079 | .1316039495 |
| C | 6.0 | -.2287365569 | .7627810307 | .1806855035 |
| C | 6.0 | .2229753866 | .9560341189 | -1.2446483890 |
| S | 16.0 | .8279380667 | -1.2849608894 | .5404098525 |
| H | 1.0 | -2.3012291730 | -.6908312984 | -1.6971813571 |
| H | 1.0 | -2.6872347919 | 1.0239709666 | -1.5913084814 |
| H | 1.0 | -2.2757221140 | .6454581387 | .8527928694 |
| H | 1.0 | -1.3032691872 | -1.0056673356 | .4320013973 |
| O | 8.0 | 1.2593012744 | 1.3948321457 | -1.6072776502 |
| H | 1.0 | -.0232221582 | 2.6992482454 | .9956672373 |
| H | 1.0 | 1.4260522239 | 1.7318739097 | 1.1486635612 |
| H | 1.0 | .0376739203 | 1.4378512296 | 2.2091438420 |
| O | 8.0 | -.5549374839 | -1.9802148032 | .5440160863 |
| H | 1.0 | 2.1326856690 | -.5814836797 | 2.4011940021 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 1.4516091688 | -2.1945125020 | 2.6399697766 |
| H | 1.0 | .4247405085 | -.7763632566 | 2.8505970572 |
| C | 6.0 | 1.2468057908 | -1.1933959831 | 2.2850244978 |

| | |
|---|---|
| Energy | -855.0282888 Hartree |
| ZPE | 0.164574 Hartree/Molecule |
| Imaginary Frequency | -1778.84 $cm^{-1}$ |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | .3430120409 | 1.7162391296 | 1.2285246894 |
| O | 8.0 | -.7262955043 | .4993940273 | -2.0624325100 |
| C | 6.0 | -1.9369149296 | .2272903985 | -1.3276868724 |
| C | 6.0 | -1.5539882923 | .3024353459 | .1431188952 |
| C | 6.0 | -.2378135726 | .8085119119 | .1888381163 |
| C | 6.0 | .2381919077 | .9745573855 | -1.2095584627 |
| S | 16.0 | .8429752529 | -1.3287628684 | .4887989558 |
| H | 1.0 | -2.2953766517 | -.7500548003 | -1.6480086673 |
| H | 1.0 | -2.6756291645 | .9852058086 | -1.5954313075 |
| H | 1.0 | -2.2957803197 | .6177140940 | .8698849650 |
| H | 1.0 | -1.3254559164 | -.9664640138 | .4419387227 |
| O | 8.0 | 1.2969493731 | 1.4306855729 | -1.5982754200 |
| H | 1.0 | -.0030142185 | 2.7367052638 | 1.0525326367 |
| H | 1.0 | 1.4302791362 | 1.7269121632 | 1.1656801825 |
| H | 1.0 | .0401360837 | 1.4342947903 | 2.2354552713 |
| O | 8.0 | -.5964295188 | -1.9795327876 | .5051431905 |
| H | 1.0 | 2.1529791389 | -.6069260249 | 2.3438527645 |
| H | 1.0 | 1.3825217993 | -2.1810243920 | 2.6548512757 |
| H | 1.0 | .4228182610 | -.6907547557 | 2.7637933598 |
| C | 6.0 | 1.2370617944 | -1.1865497485 | 2.2406233145 |

| | |
|---|---|
| Energy | -856.5654963 Hartree |
| ZPE | 0.156904 Hartree/Molecule |
| Imaginary Frequency | -956.39 $cm^{-1}$ |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -857.1716327 Hartree |

**(3R,SR) Transition State for formation of 3-methylene-4,5-dihydro-2-furanone from (3R,SR) 3-methanesuflinyl-3-methyl-4,5-dihydro-2-furanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.8848825869 | 0.8916093429 | -1.5847923549 |
| O | 8.0 | 1.0197137504 | 1.2708341141 | 1.4703814100 |
| C | 6.0 | 2.1190890848 | 0.9126004326 | 0.6405707253 |
| C | 6.0 | 1.5815191303 | 0.9589069604 | -0.7912818885 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.0982319575 | 0.7806577969 | -0.5867156002 |
| C | 6.0 | -0.1497809661 | 1.1767325265 | 0.8388947144 |
| S | 16.0 | -0.0261492794 | -1.5808796610 | -0.2975432055 |
| H | 1.0 | 2.4530594509 | -0.0779661397 | 0.9220249226 |
| H | 1.0 | 2.9154009207 | 1.6177392330 | 0.8261646862 |
| H | 1.0 | 1.7472472005 | 1.9387802903 | -1.2310812744 |
| H | 1.0 | 2.0334407467 | 0.2215610537 | -1.4412663724 |
| O | 8.0 | -1.1892539858 | 1.3896552181 | 1.3602782602 |
| H | 1.0 | -1.8327455425 | 1.2939782075 | -1.2631774851 |
| H | 1.0 | -1.0911327916 | -0.4056861317 | -1.7903964728 |
| H | 1.0 | -0.5457550714 | 1.2327543187 | -2.5515405612 |
| O | 8.0 | -0.8950687037 | -1.6357310023 | -1.5699705432 |
| C | 6.0 | -1.2050940332 | -1.7953732266 | 1.0400989219 |
| H | 1.0 | -0.6731116697 | -1.7168982467 | 1.9807629398 |
| H | 1.0 | -1.6451659361 | -2.7794497165 | 0.9499078413 |
| H | 1.0 | -1.9731963754 | -1.0364847701 | 0.9954053364 |

Energy -855.0273533 Hartree
ZPE 0.164861 Hartree/Molecule
Imaginary Frequency -1779.89 $cm^{-1}$

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.8871884668 | .8773336333 | -1.5981705587 |
| O | 8.0 | .9865995264 | 1.2619008279 | 1.4983965477 |
| C | 6.0 | 2.0892705027 | .8694221739 | .6474756565 |
| C | 6.0 | 1.5821339202 | 1.0032231914 | -.7889990845 |
| C | 6.0 | .1019370686 | .8220383575 | -.6047122178 |
| C | 6.0 | -.1941146892 | 1.1702130922 | .7993378135 |
| S | 16.0 | .0178870879 | -1.6342864068 | -.3105255534 |
| H | 1.0 | 2.3567234289 | -.1614109492 | .8868419044 |
| H | 1.0 | 2.9279817112 | 1.5198413925 | .8835667303 |
| H | 1.0 | 1.7837698784 | 2.0061106725 | -1.1746066087 |
| H | 1.0 | 2.0453118104 | .2831909662 | -1.4639275625 |
| O | 8.0 | -1.2772948738 | 1.3538821977 | 1.3307237816 |
| H | 1.0 | -1.8574123434 | 1.2384349480 | -1.2727819936 |
| H | 1.0 | -1.0913641043 | -.4243137269 | -1.7896295825 |
| H | 1.0 | -.5810501992 | 1.1826449327 | -2.5929470854 |
| O | 8.0 | -.9113132815 | -1.6331123591 | -1.5890198557 |
| C | 6.0 | -1.1453833332 | -1.7515243120 | 1.0552670119 |
| H | 1.0 | -.5704293526 | -1.7498593261 | 1.9808159181 |
| H | 1.0 | -1.7021070003 | -2.6804886924 | .9650854743 |
| H | 1.0 | -1.8175919905 | -.8959000134 | 1.0545332645 |

Energy -856.5665380 Hartree
ZPE 0.157235 Hartree/Molecule
Imaginary Frequency -978.64 $cm^{-1}$

MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -857.1731930 Hartree

**(5H) 3-Methyl-2-furanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 2.0854092174 | .4350468876 | .3443348594 |
| O | 8.0 | -1.0378935940 | -.2312733254 | 1.8819148873 |
| C | 6.0 | -.8118070964 | -1.5892719183 | 1.5152331412 |
| C | 6.0 | .5531117116 | -1.5901469642 | .8247005951 |
| C | 6.0 | .6769468165 | -.1540651725 | .2862676857 |
| C | 6.0 | -.2917972235 | .6089990135 | 1.1929197105 |
| S | 16.0 | .0634263424 | -.1730058394 | -1.4441157163 |
| H | 1.0 | -1.6025875590 | -1.8968330230 | .8502707894 |
| H | 1.0 | -.8323688365 | -2.1766960773 | 2.4214099666 |
| H | 1.0 | 1.3447010988 | -1.7669820318 | 1.5448535512 |
| H | 1.0 | .6223641264 | -2.3524569773 | .0587666887 |
| O | 8.0 | -.3534699915 | 1.7863370319 | 1.3016402977 |
| H | 1.0 | 2.4896979225 | .3184767825 | 1.3434858621 |
| H | 1.0 | 2.0776221939 | 1.4922685181 | .1169180541 |
| H | 1.0 | 2.7470264748 | -.0759384131 | -.3474315258 |
| O | 8.0 | -1.3397545761 | -.6647550808 | -1.3673230344 |
| C | 6.0 | -.0365519810 | 1.5742684465 | -1.8405779679 |
| H | 1.0 | -.6279492423 | 2.1036948568 | -1.1089450300 |
| H | 1.0 | -.5208485244 | 1.6147993133 | -2.8077298944 |
| H | 1.0 | .9553335202 | 1.9990460729 | -1.9166972203 |

Energy -855.0989793 Hartree
ZPE 0.171451 Hartree/Molecule

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -1.7358301352 | -.7600166600 | -.6266021196 |
| O | 8.0 | .3635241518 | -.3732574848 | -1.4250128750 |
| C | 6.0 | 1.5742163231 | .1881159135 | -.8969443737 |
| C | 6.0 | 1.2513349142 | .5694498531 | .5144009756 |
| C | 6.0 | -.0260521983 | .2578759636 | .7779861555 |
| C | 6.0 | -.6092381030 | -.3452893680 | -.4490542365 |
| C | 6.0 | -.8453606250 | .4208621686 | 2.0103642050 |
| H | 1.0 | 1.8571676883 | 1.0438867421 | -1.5131561647 |
| H | 1.0 | 2.3628205564 | -.5641338976 | -.9629425076 |
| H | 1.0 | 1.9666241042 | 1.0238499243 | 1.1850213825 |
| H | 1.0 | -.2703660819 | .8861729886 | 2.8077849588 |
| H | 1.0 | -1.2066625953 | -.5485379663 | 2.3518056045 |
| H | 1.0 | -1.7217360992 | 1.0327057228 | 1.7998592951 |

| | |
|---|---|
| Energy | -343.5907123 Hartree |
| ZPE | 0.104758 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -343.9640601 Hartree |

**3-Methylene-4,5-dihydro-2-furanone**

HF/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.7275444032 | .2650099975 | 1.9985896858 |
| O | 8.0 | .2088232945 | -.2666802065 | -1.3667613607 |
| C | 6.0 | 1.4895989576 | .1174570600 | -.8853463703 |
| C | 6.0 | 1.2451146924 | .8293617570 | .4531191202 |
| C | 6.0 | -.1061807384 | .2914768716 | .8383374457 |
| C | 6.0 | -.7118602709 | -.2833096858 | -.4005824599 |
| H | 1.0 | -.2863388090 | .6661506067 | 2.8938291464 |
| H | 1.0 | 1.9481535532 | .7462841221 | -1.6339409892 |
| H | 1.0 | 2.0892600138 | -.7765815077 | -.7624343538 |
| H | 1.0 | 2.0195763568 | .6175619786 | 1.1794497516 |
| H | 1.0 | 1.2002843938 | 1.9049162259 | .3104419799 |
| O | 8.0 | -1.8096278795 | -.6926572661 | -.5568997578 |
| H | 1.0 | -1.7085691609 | -.1684299531 | 2.0708381621 |

| | |
|---|---|
| Energy | -342.5609530 Hartree |
| ZPE | 0.111158 Hartree/Molecule |

MP2/6-31G(d,p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.7041502593 | .2245980038 | 2.0180103284 |
| O | 8.0 | .2079431800 | -.2331035569 | -1.4128575164 |
| C | 6.0 | 1.5049868239 | .1010104808 | -.8658274979 |
| C | 6.0 | 1.2315674302 | .8634456798 | .4352012700 |
| C | 6.0 | -.0981821768 | .2960428284 | .8286132899 |
| C | 6.0 | -.7306621056 | -.2461760796 | -.4107787127 |
| H | 1.0 | -.2491304221 | .6093105131 | 2.9197346795 |
| H | 1.0 | 2.0329472232 | .6814851888 | -1.6179672683 |
| H | 1.0 | 2.0481627449 | -.8268754551 | -.6795647299 |
| H | 1.0 | 2.0132784625 | .7163932267 | 1.1784963386 |
| H | 1.0 | 1.1425944220 | 1.9328597716 | .2344440868 |
| O | 8.0 | -1.8660211299 | -.6380071500 | -.5773268874 |
| H | 1.0 | -1.6826441927 | -.2304234511 | 2.0884626195 |

| | |
|---|---|
| Energy | -343.5790132 Hartree |
| ZPE | 0.105386 Hartree/Molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -343.9518333 Hartree |

# APPENDIX 9

## DATA FOR SULFONES IN CHAPTER 2

### MP2/6-31G(d,p) Coordinates

**Ethyl methyl sulfone (5)**

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.1464616617 | -0.4298395418 | -1.7690037172 |
| S | 16.0 | -0.3351272082 | -0.4994081859 | -0.0502835273 |
| O | 8.0 | -0.9551127730 | -1.8119573246 | 0.1817082759 |
| C | 6.0 | -1.6291188185 | 0.7334362971 | 0.0997547364 |
| C | 6.0 | -1.1451871312 | 2.1605697494 | -0.0968974968 |
| H | 1.0 | -2.0031688678 | 0.5736506165 | 1.1117010920 |
| H | 1.0 | -2.4190457215 | 0.4490263867 | -0.5953515181 |
| H | 1.0 | -0.8249208102 | 2.3410453006 | -1.1214962247 |
| H | 1.0 | -0.3121835358 | 2.3683590129 | 0.5702316026 |
| H | 1.0 | -1.9539838078 | 2.8539888078 | 0.1253772910 |
| H | 1.0 | 0.9078971589 | -1.1953972825 | -1.8962625455 |
| H | 1.0 | 0.5619827126 | 0.5469781289 | -1.9983502340 |
| H | 1.0 | -0.7126244852 | -0.6539533261 | -2.3956083983 |
| O | 8.0 | 0.8119997250 | -0.0474690969 | 0.7518877752 |

| | |
|---|---|
| MP2/6-31G(d,p) | -666.3857748 Hartrees |
| ZPE | 0.117752 Hartrees/molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -666.8143564 Hartrees |

**Transition state for 5**

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.4880679644 | 0.0405678499 | -0.7900294947 |
| S | 16.0 | -0.2336322539 | -0.3406969806 | 1.4959452835 |
| O | 8.0 | -1.5254443673 | -0.4458573735 | 2.2264761320 |
| O | 8.0 | 0.5292921402 | -1.6711039491 | 1.2093441407 |
| C | 6.0 | 0.9643426076 | 0.4387637811 | 2.5808789780 |
| H | 1.0 | 0.6024608931 | 1.4320954396 | 2.8314709383 |
| H | 1.0 | 1.9195489560 | 0.4868919305 | 2.0662176224 |
| H | 1.0 | 1.0427509602 | -0.1692096453 | 3.4786468681 |
| H | 1.0 | -1.5476121999 | 0.2248258885 | -0.6590493519 |
| C | 6.0 | -0.0195024593 | -1.1972357817 | -1.2425221664 |
| H | 1.0 | 0.1214416434 | 0.9315416521 | -0.8791896104 |
| H | 1.0 | -0.7571610276 | -1.9261916677 | -1.5532321026 |
| H | 1.0 | 0.3597548827 | -1.6928505488 | -0.0132695746 |
| H | 1.0 | 0.9153565461 | -1.2117069609 | -1.7885864284 |

| | |
|---|---|
| MP2/6-31G(d,p) | -666.2958787 Hartree |
| ZPE | 0.110281 Hartree/molecule |

MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -666.7200489 Hartree

**3-Butenyl methyl sulfone (6)**

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.2724580234 | -0.3217567583 | -0.5848371670 |
| S | 16.0 | -0.3083632323 | -0.2664846393 | 1.2077819285 |
| O | 8.0 | 1.0792500721 | -0.3603922875 | 1.6872440399 |
| O | 8.0 | -1.1698527928 | 0.8585992347 | 1.6036358112 |
| C | 6.0 | -1.1454603903 | -1.7774154630 | 1.6601477221 |
| H | 1.0 | -0.5738670781 | -2.6292947660 | 1.3022348498 |
| H | 1.0 | -2.1503416662 | -1.7722934472 | 1.2469328525 |
| H | 1.0 | -1.1892074728 | -1.7872225018 | 2.7466681051 |
| H | 1.0 | 0.2618307900 | -1.2262161215 | -0.8772490361 |
| C | 6.0 | 0.4236884312 | 0.9271620646 | -1.1263157254 |
| H | 1.0 | -1.3060960095 | -0.3826419023 | -0.9281416551 |
| H | 1.0 | 1.4472635687 | 0.9540317036 | -0.7512759345 |
| H | 1.0 | -0.0942275876 | 1.8073986347 | -0.7394364269 |
| C | 6.0 | 0.4176004101 | 0.9289371497 | -2.6248546563 |
| C | 6.0 | 1.5228161580 | 0.8617620191 | -3.3753839336 |
| H | 1.0 | -0.5538105280 | 0.9843358213 | -3.1068965150 |
| H | 1.0 | 2.5049860573 | 0.8088253884 | -2.9245071917 |
| H | 1.0 | 1.4742012915 | 0.8660494727 | -4.4547076247 |

MP2/6-31G(d,p) -743.5290841 Hartree
ZPE 0.151584 Hartree/molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -744.0339364 Hartree

**Transition state for 6**

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -1.1440232905 | 0.6330401154 | -0.8430873168 |
| S | 16.0 | -0.1378194315 | 0.2105462245 | 1.1154555644 |
| O | 8.0 | -1.0536898062 | 0.2998146244 | 2.2809655528 |
| O | 8.0 | 0.2890273816 | -1.2142651389 | 0.6505088249 |
| C | 6.0 | 1.4636190422 | 0.8592794943 | 1.5913038584 |
| H | 1.0 | 1.3459522254 | 1.9061511954 | 1.8575353078 |
| H | 1.0 | 2.1431932969 | 0.7377761331 | 0.7526963122 |
| H | 1.0 | 1.8074068293 | 0.2899305730 | 2.4516050393 |
| H | 1.0 | -2.1076451281 | 0.8065087591 | -0.3759061674 |
| C | 6.0 | -0.9032494361 | -0.5796022169 | -1.5163918362 |
| H | 1.0 | -0.6211325871 | 1.5361885418 | -1.1405587269 |
| H | 1.0 | -1.7574862147 | -1.2378015113 | -1.6324726910 |
| H | 1.0 | -0.2630224820 | -1.2046769904 | -0.4217305218 |
| C | 6.0 | 0.1522864105 | -0.6626732514 | -2.5445173716 |
| C | 6.0 | 1.2493919423 | 0.1102351338 | -2.6030071116 |
| H | 1.0 | 0.0446443928 | -1.4584283481 | -3.2737129566 |
| H | 1.0 | 1.4333481006 | 0.9065001084 | -1.8927358321 |
| H | 1.0 | 1.9872116546 | -0.0244432463 | -3.3793166278 |

MP2/6-31G(d,p) -743.4443611 Hartree

| | |
|---|---|
| ZPE | 0.144196 Hartree/molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -743.9459291 Hartree |

**Ethyl phenyl sulfone (7)**

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.0102727310 | 0.1841423802 | -0.5150737981 |
| O | 8.0 | -2.0254970383 | 1.0040870120 | 0.9416364981 |
| S | 16.0 | -1.1207363314 | -0.1497020374 | 0.8216612021 |
| C | 6.0 | -0.0638396766 | -0.1491409027 | 2.2732332809 |
| C | 6.0 | 0.9420206552 | -1.2870830073 | 2.2790337320 |
| H | 1.0 | -0.7657634744 | -0.2204296736 | 3.1055426278 |
| H | 1.0 | 0.4069252391 | 0.8334500785 | 2.3074497385 |
| H | 1.0 | 1.6327481842 | -1.2046244789 | 1.4420046987 |
| H | 1.0 | 0.4286649567 | -2.2435856254 | 2.2146020868 |
| H | 1.0 | 1.5198641748 | -1.2598211311 | 3.2012144392 |
| C | 6.0 | 1.8003118707 | 0.7104582900 | -2.5631759674 |
| C | 6.0 | 0.3624686884 | 1.5082158590 | -0.7875528563 |
| C | 6.0 | 0.5311685578 | -0.8807316374 | -1.2527642607 |
| C | 6.0 | 1.4283262102 | -0.6069574463 | -2.2861005047 |
| C | 6.0 | 1.2630744278 | 1.7654075237 | -1.8207530695 |
| H | 1.0 | -0.0891807312 | 2.3131786529 | -0.2224502758 |
| H | 1.0 | 0.2101335617 | -1.8902607721 | -1.0326627122 |
| H | 1.0 | 1.8352529742 | -1.4195882022 | -2.8739092734 |
| H | 1.0 | 1.5414239368 | 2.7860458114 | -2.0496915520 |
| H | 1.0 | 2.4969664201 | 0.9165823510 | -3.3655265369 |
| O | 8.0 | -1.6331290621 | -1.5180189483 | 0.6415911669 |

| | |
|---|---|
| MP2/6-31G(d,p) | -857.5381812 Hartree |
| ZPE | 0.170366 Hartree/molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -858.1487579 Hartree |

**Transition State for 7**

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -1.4676672510 | -.5635313500 | -2.3729079341 |
| S | 16.0 | -.2454492333 | -.9494578143 | -.4297027851 |
| O | 8.0 | -.8096431395 | -2.0335479580 | .4212773431 |
| O | 8.0 | 1.0265167141 | -1.2844053345 | -1.2731736718 |
| H | 1.0 | -.6506920175 | -1.9792492426 | -3.7361259377 |
| H | 1.0 | .4993681653 | -1.2489963853 | -2.3778963602 |
| H | 1.0 | -.0546976634 | -.2556383727 | -3.9370576737 |
| C | 6.0 | .4175023466 | .3179405787 | .6337517587 |
| H | 1.0 | -2.2601270471 | -1.2206781388 | -2.0345210305 |
| C | 6.0 | -.5133855756 | -.9991336707 | -3.2972117188 |
| H | 1.0 | -1.6556588164 | .4927872692 | -2.2236824615 |
| C | 6.0 | 1.2718219380 | 2.3738599508 | 2.2831438900 |
| C | 6.0 | -.0686039641 | .3872441419 | 1.9397347530 |
| C | 6.0 | 1.3064529269 | 1.2695032979 | .1280438089 |
| C | 6.0 | 1.7381924877 | 2.2951067138 | .9678461537 |
| C | 6.0 | .3805485736 | 1.4153625060 | 2.7694720526 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -.7521880677 | -.3719575322 | 2.2956794847 |
| H | 1.0 | 1.6802297664 | 1.1786981888 | -.8827155634 |
| H | 1.0 | 2.4379323108 | 3.0324949775 | .5958229256 |
| H | 1.0 | .0259585384 | 1.4733010689 | 3.7905276604 |
| H | 1.0 | 1.6128169079 | 3.1722847053 | 2.9294601062 |

MP2/6-31G(d,p) -857.4486277 Hartree
ZPE 0.162899 Hartree/molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -858.0545306 Hartree

**Ethylene**

| | | | | |
|---|---|---|---|---|
| H | 1.0 | 0.0000000043 | 0.9208050941 | 1.2333320210 |
| C | 6.0 | -0.0000000110 | -0.0000000941 | 0.6676402242 |
| C | 6.0 | -0.0000000007 | 0.0000000936 | -0.6676402244 |
| H | 1.0 | 0.0000000044 | -0.9208050363 | 1.2333320119 |
| H | 1.0 | 0.0000000016 | 0.9208050364 | -1.2333320118 |
| H | 1.0 | 0.0000000014 | -0.9208050937 | -1.2333320209 |

MP2/6-31G(d,p) -78.3172747 Hartree
ZPE 0.052343 Hartree/molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -78.39003 Hartree

**1,3-Butadiene**

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -2.5826149195 | 0.0725250950 | -0.4694644897 |
| C | 6.0 | -1.5222888379 | -0.1313104173 | -0.5057812966 |
| C | 6.0 | -0.7256721434 | 0.1124894346 | 0.5464859352 |
| H | 1.0 | -1.1272494502 | -0.5522108039 | -1.4204281786 |
| H | 1.0 | -1.1667062861 | 0.4839780367 | 1.4656045084 |
| C | 6.0 | 0.7256789568 | -0.1125242685 | 0.5465178480 |
| C | 6.0 | 1.5223075392 | 0.1313033190 | -0.5057747470 |
| H | 1.0 | 1.1667104881 | -0.4839677417 | 1.4655973656 |
| H | 1.0 | 1.1272236842 | 0.5521930689 | -1.4204397996 |
| H | 1.0 | 2.5826109688 | -0.0724757229 | -0.4694589455 |

MP2/6-31G(d,p) -155.4667681 Hartree
ZPE 0.086886 Hartree/molecule
MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) -155.5867097 Hartree

**Methanesulfinic acid**

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.0280548075 | 0.0217666587 | -0.3897592291 |
| S | 16.0 | -0.0751782462 | -0.2068641903 | 1.3852121910 |
| O | 8.0 | 0.7342079382 | 1.2658431724 | 1.6196299606 |
| O | 8.0 | -1.5142013000 | -0.0937673403 | 1.7466572546 |
| H | 1.0 | -0.4996897766 | -0.8057283273 | -0.8568660837 |
| H | 1.0 | 1.0700260856 | 0.0377512539 | -0.6968781505 |
| H | 1.0 | -0.4605194223 | 0.9629525256 | -0.6303093318 |
| H | 1.0 | 0.9369818469 | 1.3149802534 | 2.5673615331 |

| | |
|---|---|
| MP2/6-31G(d,p) | -588.0235297 Hartree |
| ZPE | 0.057878 Hartree/molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -588.3598417 Hartree |

**Methanesulfinic acid (G2)**

| | | | | |
|---|---|---|---|---|
| C | 6 | 0.175161 | -0.160976 | -1.511286 |
| S | 16 | 0.074820 | -0.390411 | 0.262020 |
| O | 8 | 0.878705 | 1.083022 | 0.497222 |
| O | 8 | -1.362933 | -0.280108 | 0.625172 |
| H | 1 | -0.362364 | -0.986468 | -1.980305 |
| H | 1 | 1.219238 | -0.151970 | -1.825613 |
| H | 1 | -0.309180 | 0.787300 | -1.751015 |
| H | 1 | 1.078045 | 1.140269 | 1.453181 |

G(2) Enthalpy (298 °C) -588.406426 Hartree

**Benzenesulfinic acid**

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.3302189740 | 1.5409824779 | 2.8148991595 |
| S | 16.0 | 0.5378770905 | -0.0739052962 | 1.6513170415 |
| O | 8.0 | -0.5038944411 | 1.2410096307 | 1.9067721159 |
| O | 8.0 | -0.0445420801 | -1.3482939098 | 2.1578212534 |
| C | 6.0 | 0.2113243546 | -0.0347376612 | -0.1106197753 |
| C | 6.0 | -0.1824034894 | -0.0748334732 | -2.8534899965 |
| C | 6.0 | 0.4712435746 | 1.1194976336 | -0.8524088488 |
| C | 6.0 | -0.2220051661 | -1.2115938084 | -0.7171675596 |
| C | 6.0 | -0.4309163982 | -1.2217619428 | -2.0970915368 |
| C | 6.0 | 0.2642861394 | 1.0942225956 | -2.2308865513 |
| H | 1.0 | 0.7977983680 | 2.0254006006 | -0.3585020823 |
| H | 1.0 | -0.4104631873 | -2.0836501353 | -0.1043692267 |
| H | 1.0 | -0.7789473628 | -2.1253058170 | -2.5809808332 |
| H | 1.0 | 0.4526375617 | 1.9834947583 | -2.8186738217 |
| H | 1.0 | -0.3407781089 | -0.0885570118 | -3.9242614229 |

| | |
|---|---|
| MP2/6-31G(d,p) | -779.1731538 Hartree |
| ZPE | 0.110835 Hartree/molecule |
| MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) | -779.6904968 Hartree |

CASSCF/6-31G(d,p) calculations were carried out on the transition state for **5**. The active space consisted of 5 orbitals with 6 electrons, as indicated in the main paper. Optimization was begun from the MP2/6-31G(d,p) geometry and did not result in substantial changes. Below are given the final coordinates and the occupations of the active space orbitals.

CASSCF [6,5] for the transition state of **5**

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.5059963440 | .0390596414 | -.8433791204 |
| S | 16.0 | -.2191308298 | -.3476352848 | 1.5338166077 |

| | | | | |
|---|---|---|---|---|
| O | 8.0 | -1.4814042556 | -.4353778812 | 2.2640836353 |
| O | 8.0 | .4926218611 | -1.6937415996 | 1.2444199784 |
| C | 6.0 | .9711037078 | .4381210550 | 2.6046586751 |
| H | 1.0 | .6234648478 | 1.4375389356 | 2.8281594133 |
| H | 1.0 | 1.9304402229 | .4653144106 | 2.1070968412 |
| H | 1.0 | 1.0328210686 | -.1429675471 | 3.5151802664 |
| H | 1.0 | -1.5568264670 | .1989100671 | -.6823290674 |
| C | 6.0 | -.0123214808 | -1.1979752654 | -1.2598893630 |
| H | 1.0 | .0884721033 | .9311910482 | -.9145174965 |
| H | 1.0 | -.7370010123 | -1.9289521864 | -1.5827685567 |
| H | 1.0 | .3390261398 | -1.6664479486 | -.0455165698 |
| H | 1.0 | .9182587953 | -1.1972038107 | -1.8059140096 |

Optimized CASSCF/6-31G(d,p) -665.3841718 Hartree

Natural orbital occupation numbers for the active space are: 1.975, 1.973, 1.999, and 0.027, 0.026

**Table 3. Calculated Kinetic Isotope Effects**

| Temperature (K) | $k_H/k_D$ (**8**) | $k_H/k_D$ (**9**) | average | Std. Dev. |
|---|---|---|---|---|
| | Unscaled vibrational frequencies | | | |
| 298.15 | 5.151 | 4.894 | 5.022 | 0.128 |
| 763.15 | 1.961 | 1.929 | 1.945 | 0.016 |
| 773.15 | 1.945 | 1.913 | 1.929 | 0.016 |
| 783.15 | 1.929 | 1.899 | 1.914 | 0.015 |
| 793.15 | 1.914 | 1.884 | 1.899 | 0.015 |
| 803.15 | 1.900 | 1.870 | 1.885 | 0.015 |
| 813.15 | 1.889 | 1.857 | 1.873 | 0.016 |
| 823.15 | 1.872 | 1.844 | 1.858 | 0.014 |
| | Scaled vibrational frequencies (0.9608) | | | |
| 298.15 | 4.853 | 4.621 | 4.738 | 0.116 |
| 763.15 | 1.912 | 1.882 | 1.898 | 0.014 |
| 773.15 | 1.897 | 1.868 | 1.883 | 0.014 |
| 783.15 | 1.882 | 1.854 | 1.869 | 0.014 |
| 793.15 | 1.868 | 1.841 | 1.855 | 0.013 |
| 803.15 | 1.855 | 1.828 | 1.842 | 0.013 |
| 813.15 | 1.842 | 1.815 | 1.829 | 0.013 |
| 823.15 | 1.829 | 1.803 | 1.817 | 0.013 |

# APPENDIX 10

## COORDINATES FOR SULFOXIDES IN CHAPTER 3

### Ground State Geometries

#### $H_2SO$

$C_s$ Symmetry Unique Atoms

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.6864322700 | -0.9544916729 | 0.9459929426 |
| S | 16.0 | 0.1338733637 | -0.4028519902 | 0.0000000000 |
| O | 8.0 | -0.0568278237 | 1.0701312360 | 0.0000000000 |

Energy -473.9717557 Hartree
ZPE 0.021460 Hartree/Molecule

CASSCF[14,10]/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.6801869981 | -0.9491385028 | 0.9506457352 |
| S | 16.0 | 0.1219346829 | -0.4081247887 | 0.0000000000 |
| O | 8.0 | -0.0573796867 | 1.0646976943 | 0.0000000000 |

Energy -473.6460244 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.9610427 Hartree

#### Transition state for $H_2SO$

$C_{2v}$ Symmetry Unique Atoms

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 0.0000000000 | 0.0000000000 | -1.1027849615 |
| S | 16.0 | 0.0000000000 | 0.0000000000 | 0.4010943551 |
| H | 1.0 | 1.0913476416 | 0.0000000000 | 1.1544683032 |

Energy -473.9078798 Hartree
ZPE 0.019939 Hartree/Molecule

CASSCF[14,10]/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 0.0000000000 | 0.0000000000 | -1.1113940255 |
| S | 16.0 | 0.0000000000 | 0.0000000000 | 0.4040576563 |
| H | 1.0 | 1.0853522564 | 0.0000000000 | 1.1572911846 |

Energy -473.5515262 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.9086434 Hartree

**DMSO**

$C_s$ Symmetry Unique Atoms

MP2/6-311+G(3df)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.7912020552 | -.1784228989 | -1.3326025832 |
| S | 16.0 | .2377638890 | .4420215146 | .0000000000 |
| O | 8.0 | 1.4796097779 | -.3815843044 | .0000000000 |
| H | 1.0 | -.2872579412 | .0681928511 | -2.2654848900 |
| H | 1.0 | -.8765514771 | -1.2606327751 | -1.2305252613 |
| H | 1.0 | -1.7688511599 | .3031696678 | -1.2976561350 |

Energy -552.4082868 Hartree

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.7910187332 | -0.1782999745 | -1.3326800717 |
| S | 16.0 | 0.2388376783 | 0.4422210277 | 0.0000000000 |
| O | 8.0 | 1.4795989056 | -0.3819999381 | 0.0000000000 |
| H | 1.0 | -0.2883455088 | 0.0681991148 | -2.2648802133 |
| H | 1.0 | -0.8768501724 | -1.2594472997 | -1.2306704151 |
| H | 1.0 | -1.7681796776 | 0.3019630646 | -1.2985503531 |

Energy -552.4409112 Hartree

CASSCF[14,10]/6-311+G(3df)

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.7897488995 | -.1820870817 | -1.3488504742 |
| S | 16.0 | .2287885327 | .4278022591 | .0000000000 |
| O | 8.0 | 1.4866914973 | -.3699819556 | .0000000000 |
| H | 1.0 | -.2846844999 | .0747708145 | -2.2701649483 |
| H | 1.0 | -.8878753061 | -1.2578207681 | -1.2724835332 |
| H | 1.0 | -1.7606071095 | .2987523336 | -1.3184594398 |

Energy -551.7547611 Hartree

MCQDPT/6-311+G(3df)//
CASSCF[14,10]/6-311+G(3df) Energy -552.3917166 Hartree

### Transition state for DMSO

$C_{2v}$ Symmetry Unique Atoms

MP2/6-311+G(3df)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | .0000000000 | .0000000000 | -1.8824729198 |
| S | 16.0 | .0000000000 | .0000000000 | -.3604006906 |
| C | 6.0 | .0000000000 | 1.5118929831 | .5826578708 |
| H | 1.0 | .0000000000 | 2.2889809566 | -.1811474961 |
| H | 1.0 | .8991684186 | 1.6019507138 | 1.1897386620 |

Energy -552.3250077 Hartree

MP2/6-311+G(3df,2p)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 0.0000000000 | 0.0000000000 | -1.8831367995 |
| S | 16.0 | 0.0000000000 | 0.0000000000 | -0.3614211056 |
| C | 6.0 | 0.0000000000 | 1.5105573970 | 0.5825086890 |
| H | 1.0 | 0.0000000000 | 2.2867462424 | -0.1807239932 |
| H | 1.0 | 0.8976421848 | 1.6023734006 | 1.1900225751 |

Energy -552.3574652 Hartree

CASSCF[14,10]/6-311+G(3df)

| | | | | |
|---|---|---|---|---|
| O | 8.0 | .0000000000 | .0000000000 | -1.9148463240 |
| S | 16.0 | .0000000000 | .0000000000 | -.3818355746 |
| C | 6.0 | .0000000000 | 1.5177524784 | .5822429873 |
| H | 1.0 | .0000000000 | 2.3072065794 | -.1558568934 |
| H | 1.0 | .8903577813 | 1.5880736994 | 1.1907528744 |

Energy -551.6448250 Hartree
MCQDPT/6-311+G(3df)//
CASSCF[14,10]/6-311+G(3df) Energy -552.3233388 Hartree

## Excited State Relaxed Geometries

### $H_2SO$ Singlet States

$C_s$ Symmetry Unique Atoms

CASSCF[14,10]/6-311+G(3df,2p) [$^1$A']

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -.6551547291 | -.8155139463 | 1.0145357528 |
| S | 16.0 | .1989905275 | -.7838396353 | .0000000000 |
| O | 8.0 | -.1845000694 | 1.1731634278 | .0000000000 |

Energy -473.4734186 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.8205912 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^1$A"]

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.6262128576 | -0.8381809638 | 0.9830770428 |
| S | 16.0 | 0.2753601857 | -0.7982501795 | 0.0000000000 |
| O | 8.0 | -0.1879644705 | 1.3233221071 | 0.0000000000 |

Energy -473.4587114 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.8269899 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^1$A"]

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -.7243648873 | -.9099246773 | .9635504922 |
| S | 16.0 | .2869112588 | -.5107558457 | .0000000000 |
| O | 8.0 | -.1340004843 | 1.0889011003 | .0000000000 |

Energy -473.4105165 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.7723409 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^1$A"]

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.0064222201 | -0.5938509381 | 1.3729030101 |
| S | 16.0 | -0.4980906718 | -0.6735575787 | 0.0000000000 |
| O | 8.0 | -0.1963848879 | 1.0263994549 | 0.0000000000 |

Energy -473.4550635 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.8175388 Hartree

$C_{2v}$ Symmetry Unique Atoms

CASSCF[14,10]/6-311+G(3df,2p) [$^1$B$_1$]

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 0.0000000000 | 0.0000000000 | -0.8534930835 |

| | | | | |
|---|---|---|---|---|
| S | 16.0 | 0.0000000000 | 0.0000000000 | 0.6845114456 |
| H | 1.0 | 1.5827076270 | 0.0000000000 | 0.8881138190 |

Energy -473.4879457 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.8632537 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^1B_2$]

| | | | | |
|---|---|---|---|---|
| O | 8.0 | .0000000000 | .0000000000 | -.8580341570 |
| S | 16.0 | .0000000000 | .0000000000 | .8808055224 |
| H | 1.0 | 1.4904105875 | .0000000000 | .7922373174 |

Energy -473.4453568 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.8044893 Hartree

**$H_2SO$ Triplet States**

$C_s$ Symmetry Unique Atoms

CASSCF[14,10]/6-311+G(3df,2p) [$^3A'$]

This was an unbound state (S-O cleavage).

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.6648994160 | -1.4638510061 | 0.9718824280 |
| S | 16.0 | 0.1782219884 | -1.1392245124 | 0.0000000000 |
| O | 8.0 | -0.1442421565 | 2.8252224245 | 0.0000000000 |

Energy -473.5508574 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^3A''$]

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -0.7538850545 | -0.9506674298 | 1.0619310238 |
| S | 16.0 | 0.3080951435 | -0.4340400284 | 0.0000000000 |
| O | 8.0 | -0.0961440346 | 1.0936707880 | 0.0000000000 |

Energy -473.4319518 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.8005300 Hartree

$C_{2v}$ Symmetry Unique Atoms

CASSCF[14,10]/6-311+G(3df,2p) [$^3B_1$]

| | | | | |
|---|---|---|---|---|
| O | 8.0 | .0000000000 | .0000000000 | -.8278982231 |

| | | | | |
|---|---|---|---|---|
| S | 16.0 | .0000000000 | .0000000000 | .6753048249 |
| H | 1.0 | 1.4492270996 | .0000000000 | .8799196992 |

Energy -473.5043445 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.8752624 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^3B_2$]

| | | | | |
|---|---|---|---|---|
| O | 8.0 | .0000000000 | .0000000000 | -.8236339501 |
| S | 16.0 | .0000000000 | .0000000000 | .8728670978 |
| H | 1.0 | 1.5102034349 | .0000000000 | .7790064262 |

Energy -473.4515941 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -473.8111115 Hartree

**DMSO Singlet States**

$C_s$ Symmetry Unique Atoms

CASSCF[14,10]/6-311+G(3df,2p) [$^1A'$]

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.7864256966 | -.1248461733 | -1.4060849048 |
| S | 16.0 | -.0091683600 | .6720148968 | .0000000000 |
| O | 8.0 | 1.4080840887 | -.8691252712 | .0000000000 |
| H | 1.0 | -.2672728759 | .2170963139 | -2.2896992355 |
| H | 1.0 | -.6824339909 | -1.1950969972 | -1.3228132694 |
| H | 1.0 | -1.8285011010 | .1639274937 | -1.4523784707 |

Energy -551.5692926 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -552.2394824 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^1A''$]

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.7854211222 | -0.1221081295 | -1.4019688299 |
| S | 16.0 | 0.0226096637 | 0.6766840674 | 0.0000000000 |
| O | 8.0 | 1.4090781299 | -0.9042790311 | 0.0000000000 |
| H | 1.0 | -0.2909197975 | 0.2224567318 | -2.2993782402 |
| H | 1.0 | -0.6772565249 | -1.1914541894 | -1.3096398364 |
| H | 1.0 | -1.8274222523 | 0.1674285191 | -1.4258414735 |

Energy -551.5544241 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -552.2469800 Hartree

$C_{2v}$ Symmetry Unique Atoms

CASSCF[14,10]/6-311+G(3df,2p) [$^1B_1$]

| | | | | |
|---|---|---|---|---|
| O | 8.0 | .0000000000 | .0000000000 | -1.3697751789 |
| S | 16.0 | .0000000000 | .0000000000 | .1431359230 |
| C | 6.0 | .0000000000 | 2.3088034834 | .5480061484 |
| H | 1.0 | .0000000000 | 2.6547951737 | -.4708654469 |
| H | 1.0 | .9089166192 | 2.4824343914 | 1.0978649098 |

Energy -551.6007859 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -552.2929529 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^1B_2$]

| | | | | |
|---|---|---|---|---|
| O | 8.0 | .0000000000 | .0000000000 | -1.1447197414 |
| S | 16.0 | .0000000000 | .0000000000 | .6051157566 |
| C | 6.0 | .0000000000 | 2.1054702888 | .4974445648 |
| H | 1.0 | .0000000000 | 2.3240482814 | -.5583752717 |
| H | 1.0 | .9021298873 | 2.4171231463 | .9951417962 |

Energy -551.5446866 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -552.2214235 Hartree

**DMSO Triplet States**

$C_s$ Symmetry Unique Atoms

CASSCF[14,10]/6-311+G(3df,2p) [$^1$A']

This was an unbound state (S-O cleavage).

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -.9135457547 | -.0178642703 | -1.3834137977 |
| S | 16.0 | -.1648546265 | .8594003674 | .0000000000 |
| O | 8.0 | 2.6003202939 | -1.7908087269 | .0000000000 |
| H | 1.0 | -.5391923906 | .4351332882 | -2.2919538469 |
| H | 1.0 | -.6381038197 | -1.0650978713 | -1.3753242610 |
| H | 1.0 | -1.9920666687 | .0760584830 | -1.3637623939 |

Energy -551.6319676 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^1$A"]

This was an unbound state (S-O cleavage).

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -0.9364139399 | -0.0322024134 | -1.4023670240 |
| S | 16.0 | -0.2069246412 | 0.9043748160 | 0.0000000000 |
| O | 8.0 | 2.7692381045 | -1.6929226943 | 0.0000000000 |
| H | 1.0 | -0.5720091454 | 0.4262993640 | -2.3119661498 |
| H | 1.0 | -0.6212646967 | -1.0669745948 | -1.3715024428 |
| H | 1.0 | -2.0166447497 | 0.0296770334 | -1.3788142597 |

Energy -551.6325770 Hartree

$C_{2v}$ Symmetry Unique Atoms

CASSCF[14,10]/6-311+G(3df,2p) [$^1B_1$]

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 0.0000000000 | 0.0000000000 | -1.3802101665 |
| S | 16.0 | 0.0000000000 | 0.0000000000 | 0.1253464271 |
| C | 6.0 | 0.0000000000 | 2.1249153357 | 0.5402246802 |
| H | 1.0 | 0.0000000000 | 2.5465008167 | -0.4517652559 |
| H | 1.0 | 0.9012535128 | 2.3214771972 | 1.0992616693 |

Energy -551.6058655 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -552.30560 Hartree

CASSCF[14,10]/6-311+G(3df,2p) [$^1B_2$]

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 0.0000000000 | 0.0000000000 | -1.1051571285 |
| S | 16.0 | 0.0000000000 | 0.0000000000 | 0.5439587079 |
| C | 6.0 | 0.0000000000 | 2.2299838598 | 0.4878054928 |
| H | 1.0 | 0.0000000000 | 2.4745251964 | -0.5602543332 |
| H | 1.0 | 0.9087692619 | 2.4777885177 | 1.0062994719 |

Energy -551.5564586 Hartree
MCQDPT/6-311+G(3df,2p)//
CASSCF[14,10]/6-311+G(3df,2p) Energy -552.27218 Hartree

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