Ring Strain Effects on the Interconversion of Intermediates in the Reaction of Organic Sulfides with Singlet Oxygen

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Ab initio methods are used to investigate ring strain effects on sulfide–singlet oxygen reaction intermediates. The optimized persulfoxide and thiadioxirane structures derived from 3-, 4-, and 5-membered ring sulfides showed minor albeit systematic changes in geometry. These persulfoxides and thiadioxiranes are best described as distorted tetrahedral and trigonal bipyramidal in nature, respectively. We find that the persulfoxy sulfur becomes less sulfonium-ion-like in character with decreasing ring size. In addition, the persulfoxide and the thiadioxirane are nearly isoenergetic in all cases and their interconversion barriers are nearly identical. We speculate that the anticipated ring strain effect in the persulfoxide is compensated for by a weaker sulfur–oxygen interaction and the corresponding relaxation of the need to attain the energetically preferred tetrahedral geometry.

Introduction

Intermediates formed in sulfide photooxidations with singlet oxygen ($^1O_2$) are of recent interest because of their potential synthetic utility[1,2] and importance to biological systems.[3,4] A previous study[5] of the reaction of diethyl sulfide (**1**), with $^1O_2$ in aprotic solvents indicated that both the persulfoxide **1A** and the thiadioxirane **1B** (Scheme 1) are on the reaction surface. This study laid the groundwork for understanding the electronic character of these different intermediates. Trapping studies showed that the first intermediate **1A** acts as a nucleophile and the second intermediate **1B** as an electrophile in reactions with diaryl sulfoxides and sulfides, respectively. The two intermediates are different structurally as well as electronically. The persulfoxide bears a positive charge on the sulfur, preferentially adopting a tetrahedral geometry similar to that of a sulfonium salt with a C–S–C bond angle of ca. 105°. The thiadioxirane contains a 3-membered ring with two unequal S–O bond distances, where one oxygen is apical and the other equatorial, forming a distorted trigonal bipyramidal geometry.

In a recent theoretical study[6] it was demonstrated that dimethyl persulfoxide (**2A**) and the thiadioxirane **2B** are nearly isoenergetic with a substantial interconversion barrier of 20 kcal/mol (Scheme 2A). This large barrier is undoubtedly responsible for the very small rates of chemical reaction (k_r) of sulfides with $^1O_2$ and precludes direct detection of the thiadioxirane.

In an attempt to provide more substantial evidence for a thiadioxirane intermediate, Clennan and Zhang recently examined the photooxidation of sulfenamides.[7] It

was anticipated that the electron-withdrawing nitrogen would destabilize the persulfinamide by intensifying the positive charge at sulfur while at the same time stabilize the thiadioxirane by the well-established apocophilic effect[8] (Scheme 2B). This strategy appears to have been partially successful. The diminished reactivities of the sulfenamides are consistent with destabilization of the persulfinamide; however, only circumstantial evidence for the population of a thiadioxirane was obtained.

An alternative strategy to destabilize the persulfoxide by placing the sulfur in a small ring can also be envisioned. The small ring would destabilize the persulfoxide by structurally preventing attainment of its preferred tetrahedral geometry.[9] In order to evaluate this protocol, we have calculated the relative energies of the persulfoxides and the thiadioxiranes and the magnitudes of the barriers connecting them for the 3-, 4-, and 5-membered ring sulfides (**3**, **4**, and **5**). The results of these studies are presented here.
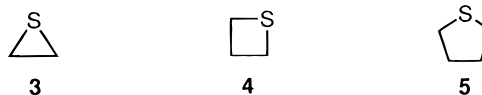
Methods

Calculations were performed using the Gaussian-92 program package.[10] Standard notations and procedures used in this paper have been described previously.[11] All geometry optimizations were done at the MP2/6-31G* level, and the nature of stationary points was verified by frequency calcula-

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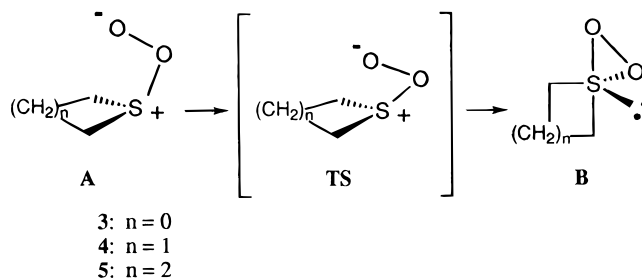
Scheme 1
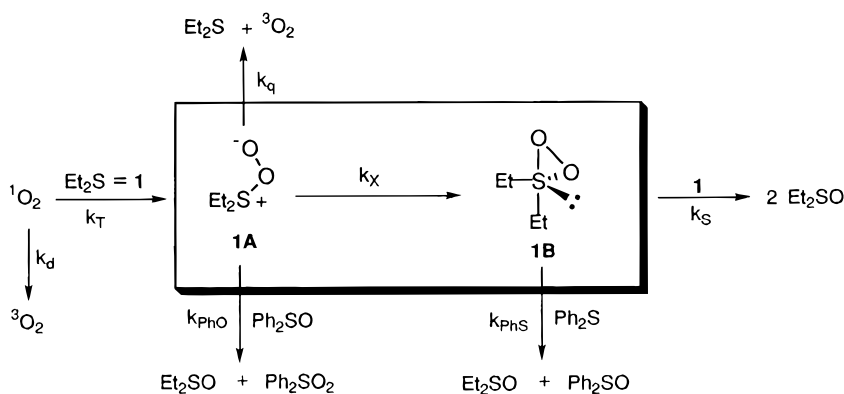
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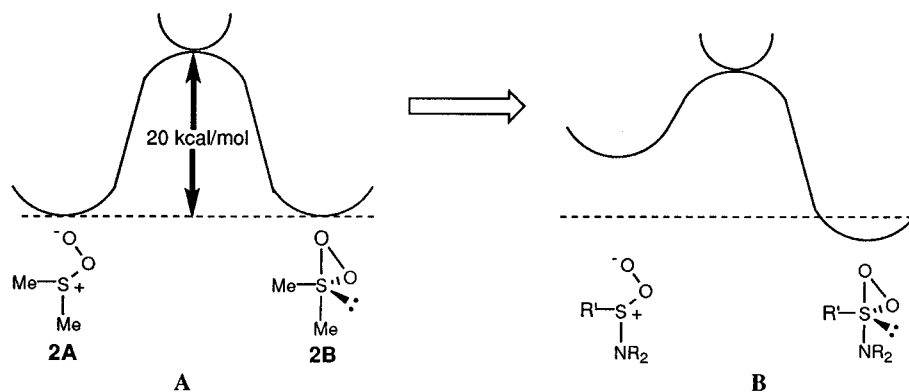
tions. Sensitivity toward inclusion of additional electron correlation was tested by running single-point calculations on optimized geometries up to either the fourth-order perturbation (MP4) or coupled cluster (CCSD(T)) level. Basis set dependence was tested by comparing the 6-31G*, 6-311G(2d), and 6-311+G(2df) basis sets.

The term singlet oxygen refers to the singlet Δ state for the isolated oxygen molecule. A correct description of the doubly degenerate Δ state requires complex orbitals,[6] but for the present systems, where a strong interaction between the sulfide and oxygen is present, a closed shell, single-determinant description is sufficient. The nature of the potential energy surface (PES) for these intermediates is different at the Hartree–Fock (HF) and MP2 levels. The energetics calculated at the HF level are not reported, since we found electron correlation necessary for this theoretical study. An earlier study also demonstrated the importance of electron correlation in the calculations of sulfide–$^1O_2$ reactions.[6] In this same study, it was shown that calculations on the dihydrosulfide–$^1O_2$ system at either the HF/3-21G* or HF/3-21G(*) levels were unsuccessful at locating a thiadioxirane minimum on the PES.[6]

Results and Discussion

The results for **3**, **4**, and **5** are discussed using the nomenclature presented in Scheme 3. Calculated geometries are shown in Figure 1 and will be discussed first, followed by the energetic results.

A. Persulfoxides. Structures **3A** and **4A** have C_s symmetry, while **5A** has no symmetry. This is a logical consequence of the underlying symmetry of the sulfides: C_{2v} for **3**, C_s for **4**, and C_2 for **5**. In all cases, the outer oxygen optimizes to a location above the methylene groups.[12]

Several features indicate that the size of the ring containing the sulfur plays an important role in the persulfoxide intermediate. As the ring size decreases

Scheme 3


3: n = 0
4: n = 1
5: n = 2

from 5 to 3, we observe a lengthening of the sulfur–oxygen (S–O) bond distance, an increase in the S–O–O bond angle, a reduction in the O–O bond distance, and a diminished positive charge at sulfur.

The effect of ring size is in particular very evident in the thiirane persulfoxide (**3A**). The S–O bond distance in **3A** (1.67 Å) is longer than those in thietane **4A**, thiolane **5A** (1.62 and 1.61 Å, respectively), or in dimethyl persulfoxides **2A** (1.64 Å, calculated in a previous study).[6] Persulfoxide S–O bonds in general are longer and consequently weaker than the S–O bonds in either alkyl sulfoxides (ca. 1.51 Å), or alkoxysulfonium salts (ca. 1.52 Å).[13a–c]

One may speculate that the inability of the sulfonium-like sulfur in these small-ring persulfoxides to attain the

(12) Density functional calculations with various functionals (SVWN, BLYP, BPW91, B3LYP, B3PW91) and the 6-31G* basis set do not predict the hydrogen persulfoxide to be a minimum on the PES. Upon attempted optimization the persulfoxide dissociates into its hydrogen sulfide precursor and oxygen.

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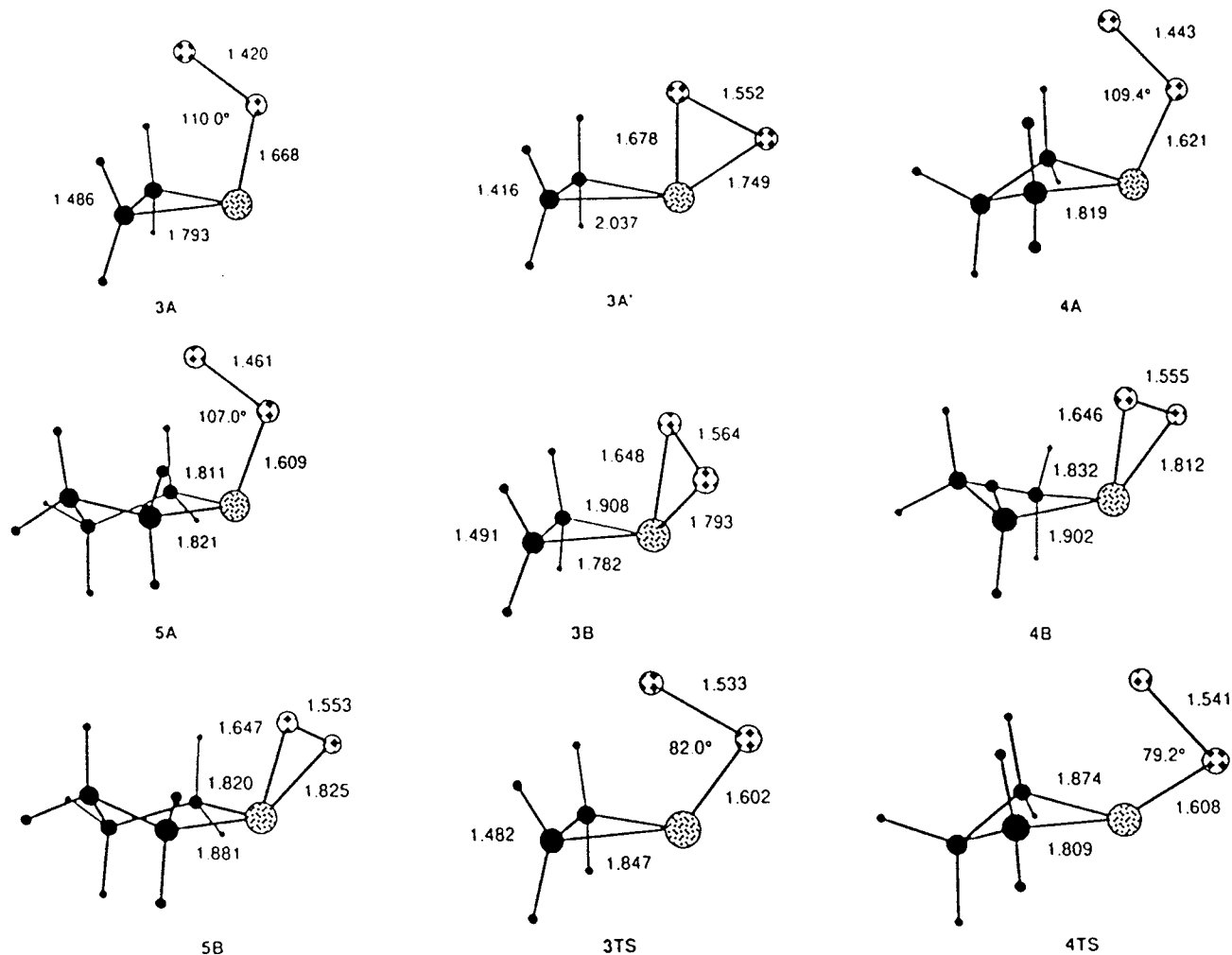
Figure 1. MP2/6-31G* optimized geometries for the **3** + $^1O_2$, **4** + $^1O_2$, and **5** + $^1O_2$ systems. Distances are in Å; angles are in deg.

geometrically preferred tetrahedral structure of their acyclic sulfonium ion analogs is compensated by a significantly diminished sulfur−oxygen interaction. This suggestion is supported by Mulliken HF/6-31G* analyses that show the positive charge at sulfur in **3A** (+0.80) is significantly reduced in comparison to that of either **4A** (+0.95) or **5A** (+0.99). Also, the Mulliken analyses reveal that the negative charge is distributed almost equally between the inner and outer oxygens (each ca. −0.50); hence, a full negative charge is not localized solely on the outer oxygen, as the drawing in Scheme 3 suggests. Since the charges on the oxygens are essentially constant, we believe that the charge difference on sulfur is due to different donation/attraction from the carbon framework.

There are interesting and unusual features of the thiirane system that make it unique in comparison to the other cyclic sulfides considered in this study. The unique character of the thiirane ring is exemplified by the observation that olefins are produced by spontaneous expulsion of elemental sulfur when impurities such as trace amounts of metal or acid are present.[14] We find that **3A** behaves differently computationally from the other persulfoxy compounds (**4A** and **5A**). When the frozen core approximation is used at the MP2/6-31G* level (correlating only the valence electrons), **3A** is apparently not a minimum on the PES. The gradient is

readily reduced to 10^{-4} au; however, upon further attempts at optimization, the structure dissociates. When the core electrons are included in the MP2 treatment, the structure shown as **3A** is obtained. Apparently **3A** is very weakly bound at this level, but larger basis sets are expected to increase the stability of **3A** relative to that of the reactants.[6] In addition to **3A**, we also find another C_s symmetric structure, shown as **3A′**. This intermediate has very long C−S bonds of 2.037 Å and S−O bond lengths (1.678 and 1.749 Å) similar to the thiadioxirane. Structure **3A′** is unique for the thiirane system. We have been unable to find similar structures for the 4- and 5-membered ring systems.

B. Thiadioxiranes. Optimized thiadioxiranes (**3B**, **4B**, and **5B**) are asymmetric with two nonequivalent S−O bonds. The geometry is best described as distorted trigonal bipyramidal, where the ligands reside in either an apical or an equatorial position. An oxygen and a carbon occupy the apical positions ($O_{a(axial)}$, C_a) leaving the remaining oxygen and carbon to occupy the equatorial positions ($O_{e(equatorial)}$, C_e). The apical bonds are longer than the equatorial bonds, as observed in the crystal structures of a large number of stable sulfuranes.[8] We find that ring strain does not dramatically affect the overall distorted trigonal bipyramidal geometry. Structures **3B**, **4B**, and **5B** bear a remarkable resemblance to each other in many of the basic geometric trends; for example, the bond distances C_a−S, S−O_e, and O−O are

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identical to within 0.03 Å in the three ring systems. Although, a small systematic increase and decrease is observed in the $S-O_a$ and $S-C_a$ distances, respectively, for ring size increases from 3 to 5.

C. Transition State Structures. We have located saddle points connecting the persulfoxide and the thiadioxirane for two of the three ring systems. Calculations were done only for the thiirane **3TS** and thietane **4TS** systems. We believe the geometric and energetic trends are so similar that calculating the larger thiolane **5TS** system is not necessary. However, **5TS** would be expected to have C_1 symmetry since its persulfoxide is C_1 symmetric in contrast to both **3TS** and **4TS** which have C_s symmetry.

The events involved in the interconversion of the persulfoxide to the thiadioxirane include the following: (1) a decrease in the $S-O-O$ angle while C_s symmetry was maintained; (2) the oxygens begin to twist (bifurcate) resulting in breaking of the C_s symmetry; (3) a new $S-O$ bond forms (perhaps by axial attack)[15] resulting in a thiadioxirane. The point of bifurcation has not been located, but must exist since a C_s symmetric persulfoxide molecule becomes an asymmetric thiadioxirane.

D. Energetic Results. Persulfoxides and thiadioxiranes are essentially isoenergetic in the gas phase. The present results show that the relative energies of the two intermediates and the connecting TS are virtually independent of ring size (Table 1). Energy values for the $2-{}^1O_2$ system previously reported[6] are included in Table 1 to help illustrate that the relative energies for our system seem to be insensitive to basis set extension.

Conclusion

In this computational study, we investigate the effect of sulfide ring size on the geometries and relative energies of intermediates formed in their reactions with

(15) A suggestion of axial attack is very tentative and cannot be shown with our systems. Unfortunately, the initial stereochemistry at the persulfoxide sulfur is not known, so possible inversion at sulfur in proceeding to thiadioxirane may not be determined. Although, a comparison can be made to the experimental study of the base-catalyzed hydrolysis of either *cis*- or *trans*-1-ethoxy-3-methylthietanium ions, where these molecules are proposed to undergo complete inversion at sulfur with hydroxide attacking from the axial position, resulting in a sulfurane intermediate prior to sulfoxide formation: Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 5644.

Table 1. Relative Energies of $R_2S + {}^1O_2$ in (kcal/mol)

	MP2			MP3		MP4		CCSD(T)
	A^a	B^b	C^c	A	B	A	B	A
2A	3.0	2.7	4.2	−4.3	−5.0	0.7	0.8	
3A	4.4	4.7		−3.3		1.7		−1.7
3A′	0.2	−1.5		0.9		−0.1		0.1
4A	2.6	2.8		−4.1		0.1		−2.6
5A	2.3	1.9						
2B	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
3B	0.0	0.0		0.0		0.0		0.0
4B	0.0	0.0		0.0		0.0		0.0
5B	0.0	0.0						
2TS	22.0	21.2	21.4	21.6	21.0	20.5	19.7	
3TS	20.8	19.4						
4TS	24.0	23.0						

^{a} Basis set A is 6-31G*. ^{b} Basis set B is 6-311G(2d). ^{c} Basis set C is 6-311+G(2df).

${}^1O_2$. The energetics of unimolecular rearrangements of the persulfoxides to thiadioxiranes are virtually independent of ring size. In addition, we do not observe any change in the persulfoxide−thiadioxirane energy difference as a function of ring size. We speculate that the anticipated change in this energy gap did not materialize in part due to a decrease in the sulfonium-ion-like character of the persulfoxide with a decrease in sulfide ring size. Persulfoxides surmount a sizable 20 kcal/mol barrier on the path to becoming a thiadioxirane. An interesting observation is that thiadioxiranes are geometrically similar to sulfuranes. This similarity features an apical−apical bond angle for thiadioxirane somewhat distorted (143°) from a trigonal bipyramidal sulfurane (180°) and two distinctly different $S-O$ bond distances.

Supporting Information Available: *Z* matrices and total energies (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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