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 thiodioxirane structures derived from 3-, 4-, and 5-membered ring sulfides showed minor albeit systematic changes in geometry. These persulfoxides and thiodioxiranes are best described as distorted tetrahedral and trigonal bipyramidal in nature, respectively. We find that the persulfoxide sulfur becomes less sulfonium-ion-like in character with decreasing ring size. In addition, the persulfoxide and the thiodioxirane 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 (1O2) are of recent interest because of their potential synthetic utility1-2 and importance to biological systems.3,4 A previous study5 of the reaction of diethyl sulfdide (1), with 1O2 in aprotic solvents indicated that both the persulfoxide 1A and the thiodioxirane 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 thiodioxirane 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 study6 it was demonstrated that dimethyl persulfoxide (2A) and the thiodioxirane 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) of sulfides with 1O2 and precludes direct detection of the thiodioxirane. An attempt to provide more substantial evidence for a thiodioxirane 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 stabilizing the thiodioxirane by the well-established apocophilic effect8 (Scheme 2B). This strategy appears to have been only partially successful. The diminished reactivities of the sulfenamides are consistent with destabilization of the persulfinamide; however, only circumstantial evidence for the population of a thiodioxirane 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 thiodioxiranes 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 calculations.
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, 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-1O2 reactions. In this same study, it was shown that calculations on the dihydrosulfide-1O2 system at either the HF/3-21G* or HF/3-21G(*) levels were unsuccessful at locating a thiadioxirane minimum on the PES.

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 Cs symmetry, while 5A has no symmetry. This is a logical consequence of the underlying symmetry of the sulfides: C2v for 3, C3v for 4, and C2 for 5. In all cases, the outer oxygen optimizes to a location above the methylene groups.

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 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 thirane 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). Persulfoxide S-O bonds in general are longer and consequently weaker than the S-O bonds in either alkyl sulfides (ca. 1.51 Å), or alkoxysulfonium salts (ca. 1.52 Å).

One may speculate that the inability of the sulfonium-like sulfur in these small-ring persulfoxides to attain the...
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. 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. In addition to 3A, we also find another Cs 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\(_{\text{axial}}\), C\(_{\text{a}}\)) leaving the remaining oxygen and carbon to occupy the equatorial positions (O\(_{\text{equatorial}}\), C\(_{\text{e}}\)). The apical bonds are longer than the equatorial bonds, as observed in the crystal structures of a large number of stable sulfuranes. 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\(_{\text{a}}\)–S, S–O\(_{\text{e}}\), 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–Oa and S–Ca distances, respectively, for ring size increases from 3 to 5.

C. Transition State Structures. We have located saddle points connecting the persulfoxide and the thia-dioxirane for two of the three ring systems. Calculations were done only for the thirane 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 C1 symmetry since its persulfoxide is C1 symmetric in contrast to both 3TS and 4TS which have Cs symmetry.

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

D. Energetic Results. Persulfoxides and thia-dioxiranes 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 2–1O2 system previously reported6 are included in Table 1 to help illustrate that the relative energies for our system seem to be insensitive to basis set extension.

Table 1. Relative Energies of R2S + 1O2 in (kcal/mol)

<table>
<thead>
<tr>
<th></th>
<th>MP2</th>
<th>MP3</th>
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<td>A</td>
<td>B</td>
<td>C</td>
<td>A</td>
</tr>
<tr>
<td>3A</td>
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<td>1.5</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
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<td>2.0</td>
<td>1.7</td>
<td>0.0</td>
</tr>
<tr>
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<tr>
<td>4TS</td>
<td>24.0</td>
<td>23.0</td>
<td>21.7</td>
<td>18.1</td>
</tr>
</tbody>
</table>

* Basis set A is 6-31G*.  B Basis set B is 6-311G(2d).  C Basis set C is 6-311+G(2df).

1O2. The energetics of unimolecular rearrangements of the persulfoxides to thia-dioxiranes are virtually independent of ring size. In addition, we do not observe any change in the persulfoxide–thia-dioxirane 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 thia-dioxirane. An interesting observation is that thia-dioxiranes are geometrically similar to sulfuranes. This similarity features an apical–apical bond angle for thia-dioxirane somewhat distorted (143°) from a trigonal bipyramidal sulfurane (180°) and two distinctly different S–O bond distances.

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

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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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