Conformationally Induced Electrostatic Stabilization of Persulfoxides: A New Suggestion for Inhibition of Physical Quenching of Singlet Oxygen by Remote Functional Groups

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Abstract: 1,5-Dithiacyclooctane is shown to chemically react more efficiently and to remove singlet oxygen from solution more rapidly than either thiane or 1,4-dithiane. These unusual characteristics of the 1,5-dithiacyclooctane reaction were explored using ab initio quantum chemical methods. A large number of persulfoxides, thiadioxiranes, and hydroperoxy sulfonium ylides were located and their structures analyzed. The unusual efficiency of the reaction was attributed to a conformational change that electrostatically stabilized the persulfoxide and increased the potential energy barrier for physical quenching.

Introduction

Schenck and Krauch reported in 1962 that singlet oxygen reacted with dialkylsulfides to give sulfoxides.1 The central mechanistic features of the reaction were described by Foote and co-workers in the 1970s and early 1980s and are depicted in Scheme 1.2−11 A noteworthy aspect of the mechanism is the sequential formation of two intermediates X and Y in aprotic solvents. The nucleophilic intermediate X partitions between efficient decomposition to triplet oxygen and dialkylsulfide in a physical quenching process, kq, adventitious trapping with sulfoxide, kSO, and rearrangement to intermediate Y, kR. The electrophilic intermediate Y reacts with starting material to generate two molecules of the sulfoxide product. The physical quenching reaction channel via X is responsible for the characteristically low quantum yields (<0.05) for sulfoxide formation in these reactions.

The past several years have witnessed a lively debate about the structural identities of intermediates X and Y.12 Persulfioxide 1 is the consensus candidate for intermediate X, and this assignment is supported by both trapping and computational studies.10,13 Discussions about the identity of Y have focused on the thiodioxirane, 2, and the hydroperox sulfonium ylide, 3. Computational studies suggest that 2 is not an energetically competent intermediate.14 On the other hand, computational studies and kinetic isotope effect studies do suggest that 3 is a viable candidate for intermediate Y.15−17 The situation is very different in protic solvents where physical quenching of singlet oxygen is completely suppressed. In these polar nucleophilic solvents both sulfuranes, 4, and hydrogen-bonded persulfoxides, 5, have been considered for the single intermediate kinetically.
required in these solvents.$^1^2$ A strong case that the identity of the intermediate is hydrogen-bonded persulfoxide, 5, has been made by demonstrating that suppression of physical quenching linearly correlates with acid strengths of protic additives.$^{18}$

In this contribution we present the unusual kinetic behavior of 1,5-dithiacyclooctane, 6,$^{19-22}$ and with the aid of computational studies we provide a unique mechanism for the reduced importance of the physical quenching channel, ($k_Q$ in Scheme 1) during its reaction with singlet oxygen. This new mechanistic suggestion for suppression of physical quenching of singlet oxygen could potentially have far-reaching implications during photooxygcnations of biological targets.

**Results**

The reaction of singlet oxygen with high concentrations (0.05–0.1 M) 1,5-dithiacyclooctane, 6, has been reported to give the sulfoxide as the primary product that further reacts to give a 86/14 mixture of the cis- and trans-(bis)sulfoxides.$^{22,23}$ At longer reaction times and lower concentrations of 6 the sulfoxide also continues to react to produce cleavage products presumably via an $\alpha$-hydroperoxy sulfoxide intermediate$^{23}$ (Scheme 2).

**Kinetics.** The rate constants for disappearance of singlet oxygen in the presence of 6, and for comparison in the presence of 1,4-dithiane, 7, and thiacyclohexane, 8, were measured by monitoring its time-resolved decay in solution at 1270 nm using standard laser flash photolysis techniques (eq 1).$^{22}$ Stern–Volmer quenching of this phosphorescent decay by different concentrations of sulfide allows separation of the sulfide induced, $k_T$, from the solvent induced, $k_d$, removal of singlet oxygen from solution (eq 2). The chemical, $k_T$, and physical, $k_Q$, rate constants for deactivation of singlet oxygen were determined by directly measuring the chemical rate constant and using the relationship, $k_T = k_Q + k_d$.

$$-rac{d[^1O_2]}{dt} = k_{obsd}[^1O_2]$$

(1)

$$k_{obsd} = k_T[^1\text{sulfide}] + k_d$$

(2)

The chemical rate constants, $k_T$, were measured using the competitive technique of Higgins, Foote, and Cheng.$^{24}$ The chemical rate constants for 6 and 8 were measured relative to that for 2,3-dimethyl-2-butene ($k_T = 2.7 \times 10^7 \text{M}^{-1} \text{s}^{-1}$)$^{25}$ and for 7 relative to that for 2,5-dimethyl-2,4-hexadiene ($k_T = 7.4 \times 10^8 \text{M}^{-1} \text{s}^{-1}$)$^{26,27}$ The $k_T$ values for 7 and 8 were determined by following product appearance by gas chromatography. However, the GC stability of the sulfoxide formed in the reaction of 6 precluded this approach and dictated monitoring starting material disappearance. A control reaction demonstrated that 6 did not react with the hydroperoxide product from the reaction of 2,3-dimethyl-2-butene with singlet oxygen. The kinetic data for all three compounds are compared in Table 1. The rate constants $k_T$ and $k_Q$ are phenomenological rate constants and are related to the microscopic rate constants given in Scheme 1 by $k_T = 2k_f(k_X)/(k_X + k_Q)$ and $k_Q = k_f(k_X)/(k_X + k_Q)$. Consequently, $k_T/k_Q$ is equal to $2x$ the fraction of intermediate X that partitions to product rather than decomposes via the physical quenching channel, $k_Q$. The comparison in Table 1 shows that 1,5-dithiacyclooctane, 6, reacts with singlet oxygen more than an order of magnitude faster than 7 and 3 times as fast as 8. In addition, chemical reaction competes with physical quenching more effectively in 6 than in either 7 or 8.

**Computational Studies.** To determine if some unique structural feature of 1,5-dithiacyclooctane is responsible for its unusual kinetic behavior we have examined 6 and 7 and their corresponding persulfoxides, thiadioxiranes, and hydroperoxy sulfonium ylides computationally. We have chosen the MP2/6-31G(d) computational method for these studies since Jensen and Foote$^{6,13}$ have shown that structural results for the singlet oxygen/dimethyl sulfoxide reaction at this ab initio level are in excellent agreement with DFT [B3LYP/6-31G(d)] calculations and with ab initio calculations with better basis sets[MP2/6-311+G(2df)] and at higher levels of theory [CCSD(T)/6-31G(d)].

There are many degrees of freedom, especially in 6 and its oxidized derivatives, and consequently we have followed the following computation protocol to ensure location of the most important stationary points. (1) Input structures for 6 and 7 were generated by placing the sulfurs at various locations in the conformations that have been identified for the hydrocarbon

| Table 1. Kinetic Data for the Reactions of 6, 7, and 8 with Singlet Oxygen$^a$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Compound       | $k_T \times 10^4$ (M$^{-1}$s$^{-1}$) | $k_Q \times 10^4$ (M$^{-1}$s$^{-1}$) | $k_R \times 10^4$ (M$^{-1}$s$^{-1}$) | $k_T/k_Q$ |
| 6              | 53              | 37.3            | 15.7            | 70             |
| 7              | 4.83            | 0.24            | 4.59            | 5              |
| 8              | 16.1            | 0.47            | 15.6            | 2.9            |

$^a$ In acetone using ($1−3) \times 10^{-5}$M Rose Bengal. 6 and 7 at 25 °C and 8 at 20 °C.

analouges, cyclooctane$^{28}$ and hexane. (2) Input structures for the persulfoxides and thiaxidooxiranes were then generated using the minimized conformations of the sulfides and placing the oxygen on the two faces of the sulfide with the pendant oxygen either bisecting the C–S–C angle or rotated by 180°. Input S–O bond lengths and S–O–O bond angles from the minimized structure of dimethylpersulfoxide were used.$^{15}$ (3) Input geometries for the hydroperoxy sulfonium ylides were generated by starting with the minimized structures of the persulfoxides and moving each hydrogen on the α-carbons to the pendant oxygen at a distance of approximately 0.98 Å. Frequency calculations to demonstrate the nature of the stationary point were conducted for all geometry optimizations.

**Sulfides.** Nine conformations of 6 were located as shown in Figure 1. The Bucourt torsional angle notation$^{29}$ is used to uniquely identify each conformation. In this notation the symbol + or − is assigned to each bond to reflect the sign of the torsional angle of the middle (2–3) bond of a four-atom segment (1–2–3–4). A positive or negative sign is assigned for right- or left-handed helical four-atom segments, respectively. The first symbol in the eight-symbol notation refers to bond 1–2 and the last symbol to bond 8–1 as defined in Figure 1. These conformations are similar to those reported earlier at a lower level of theory.$^{30}$

The two lowest-energy conformations, DTCO1 and DTCO2, have no symmetry and are best described as a twist-boat–chair and a boat–chair, respectively. A similar situation exists in cyclooctane; however, in cyclooctane the boat–chair rather than the twist-boat–chair is the global energy minimum.$^{31}$ DTCO8 is also a twist-boat–chair conformation but with the sulfurs in different positions. The twist-chair DTCO3 at 1.4 kcal/mol relative to the global minimum has $C_{3v}$ symmetry with the $o_h$ plane passing through the two sulfur atoms and the $C_3$ axis through carbons 3 and 7. The energy of the corresponding twist-chair in cyclooctane is more than 8 kcal/mol above the global minimum but suffers from severe H–H eclipsing and H–H transannular interactions absent in DTCO3.

DTCO4 is a chair–chair conformation with $C_{2v}$ symmetry with one $o_h$ plane through the sulfur atoms and the second containing carbons 3 and 7. The $C_2$ axis goes through the middle of the ring. DTCO5 and DTCO6 are boat–chair conformations with $C_{2v}$ symmetry with the $o$ plane passing through the sulfur atoms and through carbons 3 and 7, respectively. Finally DTCO7 and DTCO9 are both $C_2$ symmetric boat–boat conformations with the $C_3$ axis in the middle of the ring.

The conformational space for 1,4-dithiane, 7, is considerably less complex than that encountered for 1,5-dithiaocyclooctane, 8. The chair and the 1,4-twist-boat conformation (Figure 2) are the only minima located using either density functional$^{32}$ or MP2/6-31G(d) calculations. At the MP2/6-31G(d) level the 1,4-twist-boat ($D_2$ symmetry) is 4.79 kcal/mol less stable than the chair. All geometry optimization attempts to locate the 2,5-twist-boat conformation resulted in relaxation to form the 1,4-twist-boat. We suggest that the closer proximity of the sulfurs in the 2,5-twist-boat conformation is responsible for its absence on the conformational potential energy surface.

**Persulfoxides.** Eighteen persulfoxides derived by addition of oxygen to 1,5-dithiaocyclooctane, 6, were located as shown in Figure 3. These conformations are also uniquely identified using the Bucourt torsional angle notation. The torsional symbols (+ or −) increment in a clockwise fashion as one looks at the ring from the face bearing the peroxide linkage and begin with the sulfonium sulfur (S$^+$)-carbon bond. The Supporting Information can also be consulted for the magnitudes of the dihedral angles and other pertinent structural features.

The 18 structures differ in the conformations of the eight-membered ring, but the persulfoxide functional groups adopt a remarkably uniform local geometry. In every case the O–O bond is located above the two α-carbons nearly bisecting the C–S$^+$–C bond angle. Persulfoxides, PS2, PS4, PS5, PS9, and PS10 (Figure 3) are drawn from a perspective that allows easy visualization of this bisected geometric feature. Calculations with input geometries that placed the O–O bond at approximately 180° relative to this preferred geometry either resulted in rotation during optimization or more often collapsed to a thiaxidooxirane (vile infra). The S–O and the O–O bond lengths were between 1.59–1.65 and 1.45–1.48 Å, respectively, and the S–O–O angles were 108 ± 4°.

The eight-membered ring of the persulfoxides adopt several different structures; however, 11 of the 18 conformations are either boat–chairs or twist-boat–chairs which correspond to the two most stable conformations of cyclooctane. The most stable persulfoxide, PS1, as well as PS3, PS8, PS12, and PS14.

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Figure 2. Conformations of 1,4-dithiane and its persulfoxides, thiadioxiranes, and hydroperoxy sulfonium ylides.

are all boat--chair conformations. Surprisingly, the second most stable persulfoxide, PS2, 2.3 kcal/mol above the global minimum, is a boat--boat conformation that does not correspond to a low-energy conformation in either cyclooctane or in 6 (vide supra). PS5, PS6, PS7, PS9, PS13, and PS15, are all twist-boat--chair conformations. PS4, 3.4 kcal/mol above the global minimum, and PS10, 8.1 kcal/mol above the global minimum, are the only chair--chair, and twist-chair conformations, respectively, that are populated. PS10 has $C_1$ symmetry with the $\sigma$ plane containing both oxygen and both sulfur atoms. The remaining higher-energy conformations, PS16, PS17, and PS18, have highly distorted ring systems that have no analogue in either cyclooctane or in the parent ring system 6.

Four 1,4-dithiane persulfoxides were located as shown in Figure 2. The local persulfoxide geometry and the S--O$_1$, S--O$_2$, and O$_2$--O$_1$ distances for all four of these persulfoxides are nearly identical to those found in the DTCO persulfoxides. The two lowest-energy persulfoxides ($C_1$ symmetry) both adopt chair conformations with the axial persulfoxide, PSA, slightly more stable than the equatorial, PSE, isomer. Persulfoxides with ring systems corresponding to both the 1,4-twist-boat and 2,5-twist-boat conformations were also located. The sulfur--sulfur distance (3.27 Å) in the 2,5-twist-boat persulfoxide, 25TBPS, is considerably shorter than in the 1,4-twist-boat persulfoxide (3.54 Å). 14TBPS. Population of the 2,5-twist-boat persulfoxide suggests that oxidation at sulfur removes the destabilizing sulfur--sulfur interaction which precludes observation of this ring-conformation in the parent 1,4-dithiane (vide supra).

Thiadioxiranes. Twenty different DTCO thiadioxiranes were located as shown in Figure 4. The Bucourt torsional symbols (+ or −) in these thiadioxiranes increment in a clockwise fashion as one looks at the ring from the face bearing the short S--O (vide infra) bond beginning with the sulfonium sulfur (S$^+$)-carbon bond. The lowest-energy persulfoxide and thiadioxirane are nearly isoenergetic with an energy difference ($E_{TD1} - E_{PS1}$) of only 0.84 kcal/mol. The thiadioxiranes such as the persulfoxides also exhibit a remarkably uniform local geometry around the oxidized functional group. All the thiadioxiranes adopt a distorted trigonal bipyramidal geometry (TBP) with one long (1.88 ± 0.08 Å) and one short (1.65 ± 0.03 Å) S--O bond. In addition, all the thiadioxiranes have one short and one long S(O)--C bond ($\Delta l = 0.06 ± 0.03$ Å). The long S--O bond and long S(O)--C bond occupy the apical positions in the distorted TBP environment with an O$_{ap}$--S--C$_{ap}$ bond angle of 145 ± 4°. Longer apical than equatorial bonds, apical--S--apical angles of 180°, and equatorial--S--equatorial angles of 120° (112 ± 5° in these distorted TBP thiadioxiranes), are characteristic features of the idealized trigonal bipyramidal sulfuran. 33

TD1 and all of the thiadioxiranes DTCO ring systems that are 3 kcal/mol or less above this global minimum (Figure 4), with one exception, adopt either twist-boat--chair or boat--chair conformations corresponding to the lowest-energy conformations in cyclooctane and 6. Of these eight thiadioxiranes only TD2 adopts a higher-energy ring conformation (chair--chair in this case). TD1, TD4, TD7, TD10, TD15, and TD17 are twist-boat--chair, and TD3, TD5, TD6, TD8, TD13, TD16, and TD18 are boat--chairs. TD2 and TD11 are chair--chairs, and

only TD14 adopts a twist-chair conformation. TD9, TD14, and the two highest-energy thiadioxiranes, TD19 and TD20, are in very unusual twist-boat–twist-boat conformations (Figure 5) that have no analogous conformation in either cyclooctane or 6.

Four thiadioxiranes were located in the 1,4-dithiane system as shown in Figure 2. The lowest-energy thiadioxirane, TDC1, is 5.5 kcal/mol more stable than the lowest-energy persulfoxide, PSA. It has a local geometry reminiscent of those found in the DTCO system with one long S–O bond (1.81 Å) and one short S–O bond (1.66 Å) and a O ap–S ap–C ap bond angle of 143°.

TDC2 is an unusual thiadioxirane with C s symmetry. A similar thiadioxirane with C s symmetry was also located in the dimethyl sulfide system; however, in that case it was a transition state for interconversion of two C1 thiadioxirane minima. TDTB1 and TDTB2 adopt the 2,5-twist-boat conformation and have the anticipated distorted trigonal bipyramidal geometry (O ap–S ap–C ap bond angle of 168° and 169°, respectively). The more stable TDTB1 has the shorter S–S distance (3.20 Å in comparison to 3.39 Å in TDTB2). All attempts to locate thiadioxiranes with the 1,4-twist-boat conformation failed.

Hydroperoxy Sulfonium Ylides. Fourteen different DTCO hydroperoxy sulfonium ylides were located as shown in Figure 6. The first symbol (+ or −) in the Bucourt torsional notation for these hydroperoxy sulfonium ylides is for the S+–C2− and the last symbol for the C8−–S+ bond. The lowest-energy hydroperoxy sulfonium ylide is 12 kcal/mol more stable than the lowest-energy persulfoxide. This energy difference is remarkably similar to the MP2/6-31G(d) energy difference of 9.7 kcal/mol reported for $E_{\text{dimethylpersulfoxide}} - E_{\text{dimethylhydroperoxysulfonium ylide}}$.

The hydroperoxy hydrogens in the ylides are located above the ylide carbon C2 over a surprisingly wide range of internuclear distances between 2.04 and 3.57 Å. In those ylides with short OOH–C2 distances that are clearly inside the sum of the van der Waals radii (H, 1.20 Å; C, 1.70 Å), a weak hydrogen-bonding interaction appears to exist; however, the remarkably uniform short S+–C2− bonds (1.64 ± 0.02 Å) are indicative of substantial carbon–sulfur double bond character in all the ylides and provide evidence for lack of any covalent interaction between the OOH hydrogen and C2.

The majority of the ylides, and all of those within 5 kcal/mol of the global minimum, adopt “cis” configurations (θC8–S+–C2–C3 = 12–44°) around the S+–C2− bond. Only Y6, Y10, Y11, and Y13 adopt “trans” (θC8–S+–C2–C3 = 125–137°) but distinctly nonplanar geometries. This relative cis/trans stability is in accord with the observed 9.2 kcal/mol preference for Z in comparison to E cyclooctene.

Five different hydroperoxy sulfonium ylides were located on the 1,4-dithiane PES. The lowest-energy hydroperoxy sulfonium ylide, Y1D, is 11.9 kcal/mol more stable than the most stable persulfoxide, PSA. It adopts a somewhat distorted half-chair conformation with the hydroperoxy group in a nonbisected

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conformation and the OH group nearly anti (θ = 167°) to the S–C(sp3) bond. A second rotamer with the OH group nearly anti (θ = 178°) to the S–C(sp2) also exist but is approximately 0.8 kcal/mol less stable. Analogous nonbisected rotamers can also be located in the DTCO ylides but are approximately 1–2 kcal/mol less stable than the bisected conformations (see Supporting Information). This implies that the weak hydrogen bond present in the bisected conformations is worth approximately 1 kcal/mol. In the case of Y1D the bisected rotamer is destabilized by 1,3-diaxial interactions, overriding any energetic advantage of a hydrogen bond, and does not appear to be a minimum. The next two lowest-energy sulfonium ylides, Y2D and Y3D, both adopt bisected hydroperoxy rotamers with 1,4-twist-boat and 2,5-twist-boat conformations, respectively. Two additional hydroperoxy sulfonium ylides, Y4D and Y5D, were also located but are too high in energy to play any significant chemical role.

**Discussion**

1,5-Dithiacyclooctane, 6, in comparison to either 1,4-dithiane, 7, or thiacyclohexane, 8, exhibits an enhanced ability to remove singlet oxygen from solution, and a remarkable proclivity to chemically react rather than physically quench singlet oxygen (Table 1). The importance of transannular interactions during reactions of 6 are well established.36 Its oxidation is extremely easy, and unlike other sulfides, it exhibits electrochemically reversible behavior.37 The transannular interactions lead to formation of a S–S bond in both the radical cation and dication (Scheme 3).

We suggest that a similar transannular interaction in the persulfoxide intermediate is also responsible for the enhanced reactivity of singlet oxygen with 6. In particular, the remote sulfur atom provides anchimeric assistance during formation of the persulfoxide. The sulfur–sulfur distance in PS1 (3.16 Å), PS2 (3.03 Å), and PS4 (3.24 Å) are within the sum (3.6 Å) of the van der Waals radii34 of the two sulfur atoms. In addition, the required linear alignment of the remote sulfur and the developing S–O bond is clearly visible in the stereochemical projections of the optimized structures of all of these persulfoxides as shown in Figure 7. A similar linear alignment is not present in the optimized structures of the 1,4-dithiane persulfoxides (Figure 7) and of course is not possible in 8.

Consequently, the anchimeric assistance, $E_{AA}$, lowers the energies of the transition states for formation of the persulfoxides.

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and is responsible for the order of magnitude greater reactivity of 6 in comparison to that of 7 and the 3-fold increase in reactivity in comparison to that of 8. As anticipated the favorable electronic interaction that lowers the energy of the transition state for their formation also increases the stabilities of the persulfoxide products, PS1, PS2, and PS4, as shown in Figure 8.

The enhanced ability for chemical reaction to compete with physical quenching, \( k_q \), could be due to a smaller barrier for hydroperoxy sulfonium ylide formation (\( k_X \) in Scheme 1), or to a larger barrier for physical quenching (\( k_q \) in Scheme 1), in 6 than observed in other sulfides. We argue that a smaller barrier for hydroperoxy sulfonium ylide formation is unlikely to be responsible for this phenomenon. The local (functional group) structures of the DTCO and dimethylhydroperoxy sulfonium ylides (Figure 6) are very similar and the persulfoxide/hydroperoxy sulfonium ylide energy differences in the two systems are nearly identical. Consequently, we attribute the depressed physical quenching of singlet oxygen by 6 to an increase in the barrier for physical quenching. The origin of this barrier is a direct result of the small sulfur—sulfur distances in the energetically preferred persulfoxides, PS1 and PS2. Dissociation of these persulfoxides along the physical quenching potential energy surface encounters a significant barrier since

**Figure 6.** 1,5-Dithiaacyclooctane hydroperoxy sulfonium ylides with the hydrogens removed for clarity. The ylide (C-2) carbon is identified with a 2 in each structure.

**Figure 7.** Stereochemical projections down the O—S bond in persulfoxides.

**Scheme 3**

![Scheme 3](image)

**Figure 8.** Relative MP2/6-31G(d) energies of the persulfoxides as a function of S—S distances.

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cleavage of the S–O bond leads to the population of a highly energetic DTCO conformer with short sulfur–sulfur internuclear distances.

To obtain evidence for destabilizing sulfur–sulfur lone-pair/lone-pair interaction in the DTCO conformer formed during physical quenching we have removed oxygen from each persulfoxide and calculated a single-point MP2/6-31G(d) energy (E_{PSX} in au; $-1180.12539489$ hartrees. $^b$ Relative energies of 1,5-dithiacyclooctane in geometry found in persulfoxide PSX in kcal/mol; $E_{PSX} = -1030.22646680$ hartrees.

$^a$ Persulfide relative energies in kcal/mol; $E_{PSX}$ in au; $-1180.12539489$ hartrees. $^b$ Relative energies of 1,5-dithiacyclooctane in geometry found in persulfoxide PSX in kcal/mol; $E_{PSX} = -1030.22646680$ hartrees.

Figure 9. Relative single-point energies of persulfoxide ring systems versus the S–S distance.

stabilization due to anchimeric assistance, $E_{AA}$. The single-point energy, $E_{PSX} - E_{SS} - E_{SPE}$, and the ring energy, $E_R$, which is identical to the ring energy in the persulfoxide. Insertion of eqs 4 and 5 into eq 3 gives eq 6 which simplifies to eq 7 since lone-pair/lone-pair interaction is substantially decreased by oxidation at sulfur (i.e. $E_{PSX}^{SS} < < E_{SPE}^{SS}$). In addition, the near identical $\Delta E$’s for the persulfoxides with sulfur–sulfur distances outside of the sum of their van der Waals radii (i.e. to the right of the double line barrier in Figure 10) where both $E_{SPE}^{SS}$ and $E_{AA}$ are both zero argue that the energy of the persulfoxide functional group, $E_{SOO}$, to a first approximation, is the same in all the persulfoxides. Consequently, the linear relationship for those persulfoxides with sulfur–sulfur distances within the van der Waals radii (i.e. to the left of the double line barrier in Figure 10) must be due exclusively to variations in $E_{SS}^{PSX}$ and $E_{AA}$.

Conclusion

We have suggested that a remote functional group can enhance the rate of reactions of singlet oxygen with sulfur and stabilize the persulfoxide product, thereby increasing the quantum yield of the reaction. The novel concept that physical quenching might be suppressed by a conformational change that allows remote electron-rich functional groups to electrostatically stabilize persulfoxides and destabilize the transition state for physical quenching may have far-reaching implications, especially in biological systems.

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Supporting Information Available: Tables of structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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