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ARTICLE TYPE

Computational Investigation of the Photochemical Deoxygenation of Thiophene-*S*-oxide and Selenophene-*Se*-oxide

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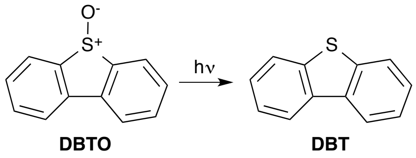
CASSCF and multireference MP2 calculations were carried out on thiophene-*S*-oxide (TO) and selenophene-*Se*-oxide (SeO), comparing the energies of the ground state to the first two electronically excited singlet and triplet states, using constrained optimizations and multiple fixed S–O or Se–O distances. For both molecules, one of the two triplet states smoothly dissociates to yield O(^{3}P) with little or no barrier. Single point calculations are consistent with the same phenomenon occurring for dibenzothiophene-*S*-oxide (DBTO). This provides an explanation for the inefficient unimolecular photochemical dissociation of O(^{3}P) from DBTO despite a phosphorescence energy below that of S-O dissociation, i.e., that S-O scission probably occurs from a spectroscopically unobserved triplet (T_2) state.

Introduction

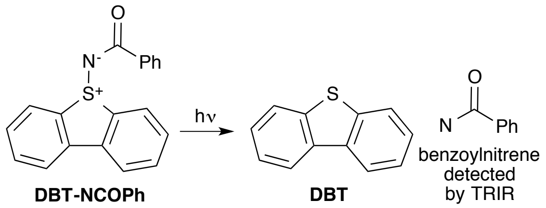
Three major unimolecular reaction pathways are common in the photochemistry of sulfoxides: homolytic S-C cleavage, stereomutation, and deoxygenation.[1-3] The latter reaction, in which the sulfoxide is transformed to the corresponding sulfide, was first reported in 1973 by Posner[4] and Davis.[5] While deoxygenation is a common minor product in photochemical reactions of sulfoxides, it can be a nearly quantitative product in the photochemistry of sulfoxides in the dibenzothiophene-*S*-oxide (DBTO) family.[4, 6-12]



Initial mechanistic proposals for photochemical sulfoxide deoxygenation focused on the formation of a transient dimeric R_2SOOSR_2 species. Decomposition of this proposed intermediate would lead to molecular oxygen, neatly accounting for the fate of the oxygen atom. Although direct evidence in favor of this dimer mechanism is sparse, support for it still appears, at least for certain substrates.[3] A second mechanistic proposal involved oxygen atom transfer from the sulfinyl radical formed after S-C cleavage, but this is now known to be energetically unfeasible.[7, 13-15]

A unimolecular dissociation mechanism resulting in the direct formation of atomic oxygen O(^{3}P) is now supported by several lines of evidence.[6-12] (1) Deoxygenation of DBTO persists at 77 K in organic glass matrices; (2) The quantum yield is independent of sulfoxide concentration; (3) Photolysis of DBTO in the presence of excess Ph_2SO does not produce Ph_2S; (4) The quantum yield is not solvent-sensitive in a manner consistent with a hydrogen abstraction mechanism; (5) Solvents are oxidized in a manner consistent with the production of O(^{3}P).

The unimolecular dissociation mechanism is not without its problems. First, there has been no direct spectroscopic detection of O(^{3}P) in the photolysis of sulfoxides in solution. However, direct time-resolved IR (TRIR) detection of benzoyl nitrene has been achieved in the photolysis of *N*-benzoyl dibenzothiophenesulfilimine (DBT-NCOPh), a structural analog of DBTO (Scheme 1).



Scheme 1. Benzoyl nitrene is detected by time-resolved infrared spectroscopy on photolysis of DBT-NCOPh.[16]

A second and more serious objection to the unimolecular dissociation mechanism is that the spectroscopically observed triplet state of DBTO (*ca*. 61 kcal/mol above ground state[17]) lies 10-15 kcal/mol below the dissociated products (72-76 kcal/mol above ground state DBTO), according to the best estimates of the bond dissociation energy (BDE) to DBT and O(^{3}P) currently available.[18, 19] Such an endothermic reaction is clearly inconsistent with reactivity at 77 K.

One solution to this dilemma is that the triplet state of DBTO is not involved in the reaction and that dissociation occurs from the exited singlet state, with intersystem crossing occurring somewhere along this dissociation pathway instead of before S–O scission. The extreme limit of this proposed mechanism is a homolytic dissociation to $DBT^{\bullet+}$ and $O^{\bullet-}$, followed by back electron transfer (Scheme 2).[10, 12]

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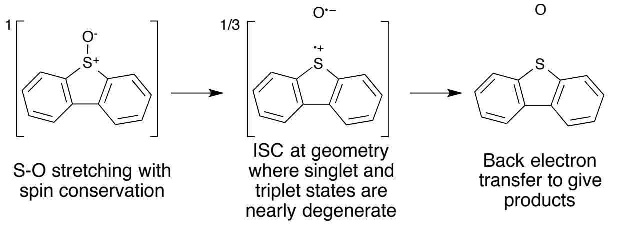
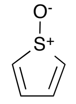


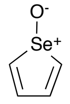
Scheme 2. A potential dissociation pathway from ^{1}DBTO to DBT + O(^{3}P).

Any reaction mechanism along this continuum would require intersystem crossing as an essential part. Experiments with halogenated DBTO derivatives did demonstrate a modest heavy atom effect, suggesting intersystem crossing could be a limiting factor in the observed quantum yield.[10] Substitution of Se for S (i.e., using dibenzoselenophene-*Se*-oxide, DBSeO) resulted in a much higher quantum yield for deoxygenation,[20-22] although this could be interpreted either as due to a heavy atom effect or as related to the fact that the Se–O bond is weaker than the S-O bond and the energetics of the reaction are more favorable.[18, 20, 22] Unfortunately, then, these results are both ambiguous.

Here we report a multireference computational investigation of S–O dissociation of thiophene-*S*-oxide (TO) and selenophene-*Se*-oxide (SeO). These molecules were chosen as models for the deoxygenation reactions because their smaller size meant that CASSCF calculations would not be nearly as onerous as proper CASSCF calculations on a molecule the size of DBTO. Moreover, although TO itself is not easily handled in the laboratory due to rapid self-condensation reactions, the photochemistry of some of its alkyl- and aryl-substituted derivatives is known. Depending on the substitution pattern, either deoxygenation (to give the corresponding thiophene) or a more complex reaction that eventually yields the corresponding *furan* predominates substituted thiophene-*S*-oxide chemistry.[23-26‡]



TO



SeO

In order to narrow the scope of required computations and focus specifically on the deoxygenation reactions, an approach was taken in which calculations would be done at various fixed S-O or Se-O distances while maintaining formal C$_s$ symmetry. These computations revealed the existence of a spectroscopically unobserved T$_2$ state beneath the singlet surfaces, from which we now believe the S–O dissociation of DBTO derivatives probably occurs.

It should be noted that there clearly is at least one bimolecular mechanism for sulfoxide photoreduction, which presumably begins with electron transfer to the sulfoxide by an external donor.[27-29] However, the current focus is on deoxygenation in the absence of other obvious reagents or sensitizers.

Computational Methods

Computations were carried out with Spartan 1.0.4.e[30] to calculate initial geometries using semiempirical methods, and GAMESS[31] for all other calculations. MacMolPlt, a graphical interface for GAMESS, was used to view all of the molecules and orbitals generated.[32] RHF and ROHF methods were used to generate orbitals for the singlet states and triplet states, respectively, of thiophene-*S*-oxide and selenophene-*Se*-oxide. The coordinates and orbitals obtained from the HF methods were used as initial coordinates and initial guess orbitals for the active space of the CASSCF calculations. The active space, which had 18 electrons in 14 orbitals, included the orbitals of the three lone pairs of electrons on oxygen, one lone pair of electrons on sulfur (or selenium), the S-O (o Se-O) σ and σ* orbitals, the C-S (or C-Se) σ and σ* orbitals, and the four C-C π and π* orbitals (Supporting Information). All fully optimized geometries were confirmed as minima by calculating the vibrational frequencies. Corrections to the CASSCF energies were made using multireference MP2 methods, as implemented in GAMESS.[33, 34]

Many calculations were carried out with the modest 6-31G(d) basis set. However, it is known that the energies of sulfoxides and other oxides of sulfur are significantly overestimated relative to their isomers in the absence of tight d-polarization functions.[15, 35-47] Thus, use of a larger basis set, such as the aug-cc-pVT(T+d)Z, is highly desirable. However, the correlation consistent basis sets are sufficiently large to make this very costly. Instead, the G3Large basis set,[48, 49] which shares many of the characteristics with respect to the d-functions, but is smaller overall, was used. Furthermore, the G3Large basis set was used only on S (or Se) and O, whereas the C and H atoms remained represented by the smaller 6-31G(d) basis set. This combination of G3Large on S (or Se) and O and 6-31G(d) on C and H will henceforth be designated G3Large*. Coefficients and exponents for the G3Large basis set for selenium, sulfur, and oxygen were obtained from http://chemistry.anl.gov/compmat/g3theory.htm.

The absolute energies obtained from CASSCF/G3Large*//CASSCF/6-31G(d) and sample CASSCF/G3Large* calculations were found to be sufficiently close to one another (Supporting Information), that all subsequent calculations with the G3Large* basis set used the optimized coordinates from the CASSCF/6-31G(d) calculations. The single point energy calculations were thus performed at CASSCF/G3Large*//CASSCF/6-31G(d) and MRMP2/G3Large*//CASSCF/6-31G(d). All energies reported in this study are the total electronic energy and do not include entropy, the zero-point energy, or temperature corrections.

Full potential energy surfaces were not deemed practical, and instead, a series of constrained optimizations was performed in which the S-O or Se-O distance was held constant but all other coordinates were optimized within Cs symmetry. The constrained optimizations were performed independently for each state located in the potential energy surface. Fully positive, definite Hessians were obtained for minima that were fully optimized on the ground state and the ^{3}A" state.

Additionally, the ground state of DBTO was optimized at CASSCF/6-31G(d) and constrained optimizations were obtained for the first four electronic states at the optimized ground state S-O distance with CASSCF/6-31G(d). The active space used was the same size as that for thiophene-*S*-oxide, i.e., 18 electrons in 14 orbitals. The same population of S and O orbitals was used as before, along with the two highest occupied and two lowest unoccupied orbitals of the π system. Single point energy

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calculations on the aforementioned states were performed at MRMP2/6-31G(d)//CASSCF/6-31G(d), CASSCF/G3Large*//CASSCF/6-31G(d), and MRMP2/G3Large*//CASSCF/6-31G(d) using the same active space.

Results and Discussion

Thiophene-*S*-oxide (TO)

An optimized ground state (S_0) structure for TO was obtained at CASSCF/6-31G(d) in Cs symmetry. As expected, some of the bond lengths are slightly overestimated at this level of theory, compared to a crystal structure for 2,5-diphenylthiophene-*S*-oxide.[50‡‡] (A table giving the major geometric parameters appears in the Supporting Information.) For example, the optimized S-O distance is 1.510 Å, whereas the experimental distance is 1.484 Å. As known in the experimental system, the sulfur atom is slightly displaced from the plane of the carbon atoms on the side opposite of that where the O atom is found (A plot indicating the angle of S displacement as a function of S-O distance for the ground state appears in the Supporting Information.). For ground state TO, the HOMO is the a” π orbital, with the next two lower orbitals (HOMO-1 and HOMO-2) being a’ and a” orbitals that are primarily lone pairs on the oxygen atom, respectively. The LUMO and LUMO+1 are π orbitals of a’ and a” symmetry respectively.

With the ground state structure in hand, geometry optimizations were attempted for structures in each of the next four electronic states ($S_1 = {}^1A'$, $S_2 = {}^1A''$, $T_1 = {}^3A''$, $T_2 = {}^3A'$). A minimized structure was obtained only for the ${}^3A''$ (T_1) state. Attempted optimization of the others led to dissociation of the S–O bond. As elaborated on below, partial optimizations, constrained only for S–O distance and symmetry, were carried out for all five electronic states.

The ${}^3A''$ optimized structure has a similar geometry to the S_0 (${}^1A'$) state. The singly occupied orbitals (natural orbital occupation numbers [NOON] of 1.024 and 0.980) are nominally the second and third π orbitals (a' and a'') of the butadiene system, making this a simple ππ* state. The most notable differences from the S_0 (${}^1A'$) geometry are the position of the sulfur atom, which is tipped slightly above the plane of the ring in this structure, and the alternation of the C-C bond lengths in the ring.

A fully optimized structure of the ${}^3A'$ (T_2) state of thiophene-*S*-oxide could not be obtained because the surface is dissociative with respect to S-O cleavage. A constrained optimization with an S-O distance of 4.00 Å (representing nearly complete dissociation) yielded the dissociated products, thiophene and O(${}^3P$); the singly occupied orbitals (NOON of 1.000 and 1.000) are the a' and a'' lone pair orbitals on oxygen. Experimental values for the structure of thiophene are compared to this geometry of the thiophene moiety the geometric table in the supporting information.

When the geometry of the ${}^3A'$ state is constrained to a 1.50 Å S–O distance, the two singly occupied orbitals (NOON of 1.026 and 1.007) are the a’ lone pair on oxygen and the a’ π* orbital of the butadiene, i.e., an $n_O\pi^*$ state. Constrained optimizations of the ${}^3A'$ state for S–O distances between 1.5 and 2.0 Å had geometries with the O atom approximately positioned as if the bond had simply been stretched. At 2.1 Å and longer, the O projects straight out from the thiophene (C_{2V} symmetry). We assume, since there is no particular discontinuity in the energies, that this reflects a very loose potential for the position of the O atom in this range.

The excited ${}^1A'$ (S_1) state also did not optimize to a minimum when starting from the ground state geometry, although the constrained optimizations indicate a minimum does exist near 1.7 Å. The structure with an S–O distance of 1.50 Å has both the sulfur and oxygen atoms on the same side of the carbon plane and singly occupied orbitals comprising the a' lone pair on oxygen and the a' π* orbital of the ring (i.e. the $n_O\pi^*$ state).

The ${}^1A''$ (S_2) state does not have an accessible minimum energy structure at the CASSCF/6-31G(d) level of theory either. A constrained optimization with the S-O distance at 1.51 Å yielded a structure with sulfur and oxygen on the same side of the carbon plane, with singly occupied orbitals comprising the a'' lone pair on oxygen and the a' π* orbital of the ring (i.e. another $n_O\pi^*$ state). As the S–O distance increases, the a'' orbital transforms smoothly from being mixed with an a'' element of the thiophene π system to residing nearly entirely on the oxygen atom. Similarly, as the S-O distance increases to 2.2 Å the singly occupied a' orbital smoothly shifts from a π orbital lightly mixed with an oxygen-centered p-component to being mainly the oxygen-centered p orbital with slight mixing from the π system.

The data obtained from the constrained optimizations allows us to test the mechanistic hypothesis put forward in Scheme 2, i.e., that separation would be homolytic, with charge separation in the singlet state followed by back electron transfer coupled to isc.

Mulliken charges obtained at a modest basis set, such as 6-31G(d), can be used as a qualitative guide to determine if charge separation has a maximum along any of the electronic surfaces through the bond stretching process, even if the absolute numbers are subject to the definition of the method.

The data in Figure 1 indicate that none of the four excited states shows a distinct maximum of charge separation at any distance beyond the equilibrium S-O bond distance of 1.51 Å. We reason that the proposed mechanism in Scheme 2 ought to be accompanied by local maxima in charge separation as the S-O distance is increased. It might reasonably be argued that these gas phase calculations substantially inhibit charge separation because of its energetic cost. However, it is also the case that, experimentally, there is little if any effect of solvent polarity on the efficiency of the photochemical reaction, as might be expected if charge separation were important. We thus tentatively conclude that charge separation is not the mechanism that drives intersystem crossing and look for another explanation.

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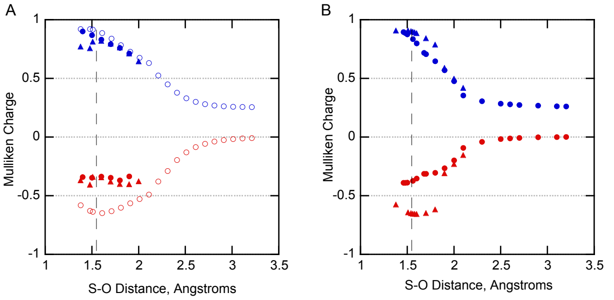

Figure 1. Mulliken charges on sulfur (blue) and oxygen (red) of thiophene-*S*-oxide as a function of S-O distance. Open circles are for lowest energy A' states (S$_0$), filled circles for an excited A' state, and triangles are for A" states. (a) Singlet states. (b) Triplet states.

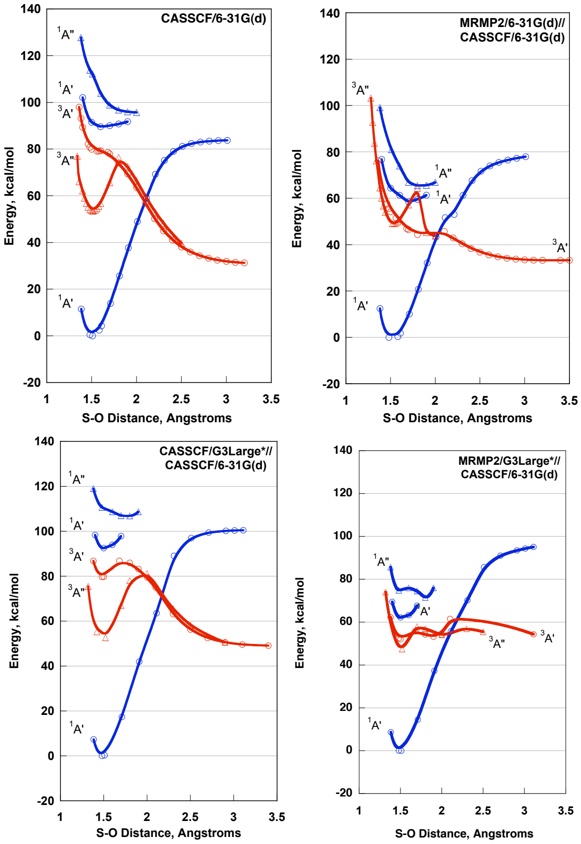

Figure 2. Energies of the electronic states of thiophene-*S*-oxide as a function of S-O separation at four levels of theory. Circles are A' states. Triangles are A" states. Singlets are blue and triplets are red, e.g., the ^{1}A' state is a blue circle.

A preliminary energy map was created from optimized CASSCF/6-31G(d) structures and energies (Figure 2, upper left). The ground state ^{1}A' state of the sulfoxide smoothly correlates to separated thiophene plus O(^{1}D) – some 84 kcal/mol uphill – at distances that approach 3 Å. The natural orbital occupation numbers in the optimized active space are all very near 2 or 0 until the oxygen atom begins to achieve substantial separation from the thiophene at ca. 2.5 Å. At the infinite separation limit, each oxygen lone pair (p orbital) would have a 1.33 occupation, and the data begin to trend in this direction as the separation gets longer. The remaining orbitals at longer distances correspond to expectations for thiophene, and have occupancies near 2 or 0.

The two triplet states are nearly degenerate at S-O distances of about 1.8 Å and longer. Both correctly correlate to the dissociation limit of thiophene plus O(^{3}P), giving an apparent S-O (electronic-only) BDE of about 35 kcal/mol at this level of theory.

At shorter S-O distances, the story is more interesting. The appearances of the energy profiles of both triplet states are strongly suggestive of an avoided crossing between a state that is dominant at short distance and what could be described as the "large separation" state that correlates with thiophene and O(^{3}P). As with the energy profile, the avoided crossing is more dramatically observed in the singly occupied orbitals of the ^{3}A" state than for the ^{3}A’. At 1.5 Å, the ^{3}A" state may be reasonably described as a $\pi\pi^*$ state – analogous to that of cyclopentadiene – with some admixture of an O p-type component to the a' orbital. As the distance grows to 1.8 Å, the admixture of the O a' component slowly and smoothly increases. Also, a p-type O-centered lone pair slowly grows in to the a" singly occupied orbital. However, at 1.9 Å, the contribution of the O-centered components is dramatically larger, particularly for the a" orbital. The discontinuity in the smooth orbital progression is *not* – as is sometimes observed with avoided crossings – accompanied by contributions to the orbitals by entirely different parts of the molecule. The singly occupied orbitals for the ^{3}A" state at 1.8 and 1.9 Å S-O separation are illustrated in Figure 3.

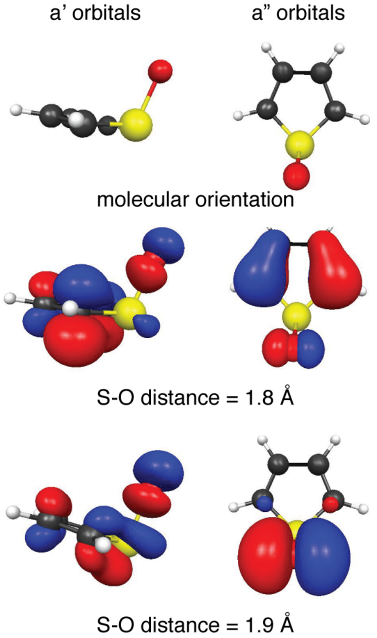

Figure 3. Singly occupied orbitals for the ^{3}A" state of thiophene-*S*-oxide at S-O distances of 1.8 and 1.9 Å, illustrating the avoided crossing also observed from the energy plot in Figure 2. Orbitals are illustrated at the 0.05 contour.

Increasing the quality of the basis set is expected to make the apparent S-O BDE larger because including the tight d functions causes the calculated energy of the oxides of sulfur to drop more

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than isomeric structures. Indeed, this is observed (Figure 2, bottom vs. top). The energy difference between thiophene and O(^{3}P) vs O(^{1}D) remains approximately 45 kcal/mol as expected, but the low energy dissociation goes up to almost 50 kcal/mol, an increase of about 15 kcal/mol due to the change in basis set alone.

It is also well understood that CASSCF excited state energies can be grossly overestimated,[51] and thus the energies were refined at the MRMP2 level (Figure 2, left vs. right). The energies of all the excited states, except ^{3}A", are lowered dramatically.

Adding in the basis set correction (i.e., MRMP2/G3Large*//CASSCF/6-31G(d,p), Figure 2 lower right) has its most dramatic effect on the two triplet states, making them closer to degenerate. The potential for the ^{3}A" state is no longer smoothly dissociative, but has very small barriers on a fairly flat dissociative surface. The ^{3}A' state still gets to the same long S-O distance energy, but has a more significant barrier to overcome before getting to that point.

Because of the appearance of the potential surfaces, the possibility of so-called intruder states was investigated.[52-54] Sample points were investigated at slightly varying distances. No evidence for highly divergent state energies, nor for additional dramatic changes in NOON or orbital appearances was noted, although a comprehensive search was not performed after preliminary sample computations did not turn up any anomalies.

The asymptotic energy limit at long S-O distances between the singlet and triplet manifolds should correspond to the energy difference between O(^{1}D) and O(^{3}P), which is experimentally known to be 45.4 kcal/mol.[55] The data in Table 1 illustrate the calculated energy gap between these two states for each of the computational methods, which vary around the experimental enegy by about 5 kcal/mol. Comparison of the singlet and triplet state energies of a system with partially filled degenerate orbitals is a particularly difficult problem. In order for computations to get this number to within 1-2 kcal/mol, extensive multireference CI calculations with larger basis sets are required. Such calculations are clearly impractical for the larger system at hand. Moreover, the relevant conclusions of this paper derive from the general shape of the triplet surfaces (same multiplicity) in the range where the S-O distance retains partial bonding (non-degenerate orbitals); thus, while the one quantitative comparison to experimental data we can make is disappointing, we do not believe that it substantially affects the conclusions we draw here.

Table 1. Calculated BDE from TO to thiophene and O(^{3}P) and O(^{3}P)-O(^{1}D) energy differences at various levels of theory (kcal/mol)

Method	BDE[a]	ΔE O(^{1}D)-O(^{3}P)
CASSCF/6-31G(d)	31.3	51.8
MRMP2/6-31G(d)// CASSCF/6-31G(d)	33.3	44.4
CASSCF/G3Large*// CASSCF/6-31G(d)	49.1	49.6
MRMP2/G3Large*// CASSCF/6-31G(d)	1	40.8
Experimental[55]		45.4

[a] Electronic energy to dissociate to thiophene and O(^{3}P). All energies in kcal/mol.

The experimental BDE of thiophene-*S*-oxide is not known with certainty. In part, this is due to the computational difficulty cited above. We recently estimated it to be near 61 kcal/mol, though a range of 56-65 kcal/mol was obtained, depending on the method.[18] MRMP2/G3Large*//CASSCF/6-31G(d,p) calculations from the current study estimate the BDE to be 54.3 kcal/mol (Table 1). Despite the acknowledged limitations, we draw a plausible, qualitative conclusion: that there is a "phantom" T_2 state for thiophene-*S*-oxide from which deoxygenation can occur with little barrier.

Selenophene-Se-oxide (SeO)

As with DBTO, dibenzothiophene-*Se*-oxide (DBSeO) undergoes efficient photochemical deoxygenation.[22] In the same spirit as for comparing the parent thiophene sulfoxide to its dibenzannulated derivative in computational means, we examined selenophene-*Se*-oxide (SeO).

A CASSCF/6-31G(d) optimization of SeO resulted in an Se-O bond length of 1.65 Å in the ground state. Like TO, both the selenium and oxygen atoms deviate from the plane of the ring carbons and are on the opposite side of one another. For the optimized ground state structure (S_0), the two highest occupied molecular orbitals, according to the preliminary Hartree-Fock calculations, are the a' and a" π orbitals (HOMO-1 and HOMO) respectively. This is distinct from TO, where the HOMO-1 is a lone pair. The two lowest unoccupied orbitals for SeO were the π-system orbitals of a' and a" symmetry.

Results from excited state calculations at different Se-O distances were in qualitative agreement with the results obtained for TO, though the precise energies of course varied. The results are illustrated in Figure 4. As with TO, only the ^{3}A" state has a minimum at the CASSCF level, so the data in Table 2 include the energies (relative to ground state) at a fixed Se-O distance of 1.65 Å for the first four excited states.

Table 2. Energies (kcal/mol) for the excited states of selenophene-*Se*-oxide, relative to the ground state,[a] and the Se-O BDE.

Method	T_1 (^{3}A") energy	T_2 (^{3}A') energy	S_n (^{1}A') energy*	S_n (^{1}A") energy*	BDE
CASSCF/6-31G(d)	53.2	80.6	89.7	103.5	26.2
MRMP2/6-31G(d)// CASSCF/6-31G(d)	49.4	51.3	61.3	71.9	29.6
CASSCF/G3Large*// CASSCF/6-31G(d)	52.5	83.6	92.5	106.2	38.9
MRMP2/G3Large*// CASSCF/6-31G(d)	47.0	52.3	55.2	52.3	44.1

[a] All calculations were performed at a constrained Se-O distance of 1.65 Å. "S_n" notation used to highlight the interchange of state energies depending on computational method.

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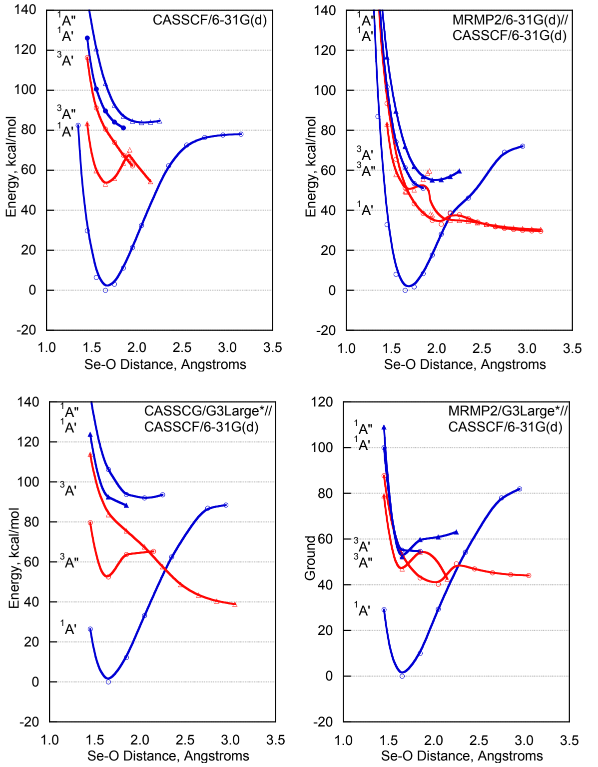

Figure 4. Energies of the electronic states of selenophene-*Se*-oxide as a function of Se-O separation at four levels of theory. Circles are A' states. Triangles are A" states. Singlets are blue and triplets are red, e.g., the ^{1}A' state is a blue circle.

Like thiophene-*S*-oxide, the T_1 state of selenophene-*Se*-oxide is a $\pi\pi^*$ state, while the T_2, S_1, and S_2 are $n_o\pi^*$ states. The Se-O BDEs estimated by these calculations (Table 2) are lower than previous estimates of approximately 57 kcal/mol.[18] Regardless, dissociation with little to no barrier is again plausible.

Dibenzothiophene-*S*-oxide (DBTO)

Thiophene-*S*-oxide and selenophene-*Se*-oxide are sufficiently small to perform a series of energy calculations with a full appropriate active space at the MRMP2/G3Large*// CASSCF/6-31G(d) level for many S-O and Se-O distances, as we report above. However, the scaling of CASSCF calculations made even a single analogous full calculation on DBTO (which would be 26 electrons in 18 orbitals) impractical with our resources.

However, to make the most direct connection from the DBTO experimental data to the current calculations, we did carry out a limited set of computations on this parent compound. The same size active space was used for DBTO as with TO and SeO. In practice this meant that only the highest two occupied π orbitals and the lowest two unoccupied ones were included, rather than the full π system. Furthermore, because of the limitations for even calculations of this size, we restricted the computations obtained for DBTO to optimizing the ground state geometry and conducting constrained optimizations for the four relevant excited states with the S-O distance held at the ground state distance. Each of these was followed up by single point energy computations up to MRMP2/G3Large*//CASSCF/6-31G(d). Table 3 gives the results of these calculations. Again, two triplet states are observed between the ground and first excited state. Of particular note is the result that the ^{3}A" (T_1) state is found to be 65.5 above the ground state, which is in reasonable agreement with the estimate of approximately 61 kcal/mol taken from phosphorescence data[17] (especially considering the lack of complete relaxation of the excited state geometry). According to the calculations, the ^{3}A' (T_2) state is about 5 kcal/mol higher than T_1 in energy.

Table 3. Energies (kcal/mol) for the excited states of DBTO, relative to the ground state and the S-O BDE.[a]

Method	^{3}A" energy	^{3}A' energy	^{1}A' energy[a]	^{1}A" energy[a]
CASSCF/6-31G(d)	76.9	101.3	101.1	120.5
MRMP2/6-31G(d)// CASSCF/6-31G(d)	64.9	74.9	79.3	78.7
CASSCF/G3Large*// CASSCF/6-31G(d)	97.2	98.7	99.7	114.4
MRMP2/G3Large*// CASSCF/6-31G(d)	65.5	69.9	72.2	67.2

[a] A fixed S-O distance of 1.51 Å was used for all calculations.

In order to answer whether that 70 kcal/mol is enough to break the S–O bond in DBTO, we need a reasonable estimate of the BDE. Our previous best estimate based on empirical corrections to computations was 72.7 kcal/mol.[18] However, we note that the number obtained by that method for thiophene-S-oxide is 6.6 kcal/mol larger than the BDE obtained using the current MRMP2/G3Large*//CASSCF/6-31G(d) calculations. Applying a "correction" of that magnitude to DBTO gives an apparent BDE of about 66 kcal/mol. (The analogous "correction" is even larger for selenophene-*Se*-oxide.)

While this estimate of the BDE remains an extrapolation, these data imply that photochemical deoxygenation of DBTO with a very low barrier is energetically plausible from the ^{3}A' (T_2) state, consistent with the more complete finding shown for thiophene-*S*-oxide.

Conclusions

Using CASSCF and MRMP2 energy calculations with a G3Large basis set on both S/Se and O and a 6-31G(d) basis set on C and H, slices of the potential energy surfaces of thiophene-*S*-oxide and selenophene-*Se*-oxide deoxygenation have been modelled as a function the S-O and Se-O bond length. Two low lying triplet excited states — both lower in energy than S_1 — have been observed. At the CASSCF level, one of these has a minimum energy structure and probably corresponds to the weakly phosphorescent triplet of DBTO. The other does not optimize, other than to O(^{3}P) and TO or SeO. After energy refinement by using multireference MP2 and an improved basis set, it remains the case that dissociation along the triplet manifold can occur with little or no barrier. Calculations could not be carried out as extensively for DBTO itself, but the presence of both low energy triplet states was verified.

Extrapolation of these results provides a consistent framework in which to understand several observations about photochemical deoxygenation: (1) The quantum yield for deoxygenation of

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DBTO is low because it probably occurs from T_2. (2) The quantum yield for deoxygenation of DBTO is wavelength-sensitive because intersystem crossing dynamics from different singlet states affect the partitioning of molecules into a dissociative T_2. (3) The quantum yield for dibenzoselenophene-*Se*-oxide is an order of magnitude higher than the maximum observed for DBTO because both low lying triplets are probably energetically above the requirement for Se-O dissociation. Finally, previous computational work[18] suggests that the BDEs for sulfoxides are generally larger than those for analogous sulfonium ylides or sulfilimines, which again is consistent with the relatively high observed quantum yields seen in the photolysis of such compounds to give nitrenes and carbenes.[16, 56-58]

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Notes and references

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† Electronic Supplementary Information (ESI) available: geometries and absolute energies of compounds. See DOI: 10.1039/b000000x/

‡ Although the mechanism for the formation of the furan is not well established, all workers currently suggest that it begins with C-S cleavage followed isomerization of the sulfoxide to make the cyclic sulfenic ester.

‡‡ Due to a fortuitous cancellation of errors, the S-O bond length of sulfoxides is well reproduced at RHF/6-31G(d). The bond length is reduced with a higher quality basis set.

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