Articles

Photochemistry and Photophysics of Halogen-Substituted Dibenzothiophene Oxides[1]

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Dibenzothiophene-5-oxide (**DBTO**) cleanly produces dibenzothiophene (**DBT**) on direct photolysis, but with very low quantum yield. A proposed mechanism involves scission of the S−O bond which is coupled to an intersystem crossing step, thus producing the sulfide and O(^{3}P) via a unimolecular pathway. To test this hypothesis, heavy atom substituted DBTOs were prepared and photolyzed. Iodo-, bromo-, and chloro-substituted DBTOs show higher quantum yields for deoxygenation than does the parent molecule, in the order consistent with an intersystem crossing-related heavy atom effect. 2-Iododibenzothiophene also undergoes photochemical deiodination. Phosphorescence data are consistent with heavy-atom assisted intersystem crossing.

Introduction

One of the fundamental photochemical reactions of aromatic sulfoxides is deoxygenation to form the corresponding sulfide on direct irradiation.[2−12] Though the sulfide is usually a minor component of the product mixture, in the photolyses of dibenzothiophene-5-oxide (**DBTO**) and some of its derivatives, it is the major sulfur-containing product.[3,13−16] From a mechanistic perspective, many experimental results are consistent with simple S−O cleavage that yields the sulfide and O(^{3}P).[13,14,16] For example, product studies based on the oxidation of solvents and other reactive traps in the presence of **DBTO** are consistent with expectations for O(^{3}P). Though no direct evidence has been obtained for the formation of this reactive intermediate, the evidence pointing toward a unimolecular mechanism is compelling.[10,13,16]
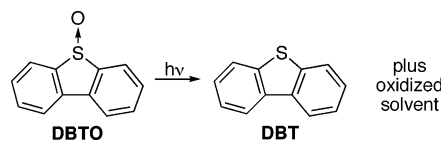
Thus, **DBTO** derivatives are promising candidates as photochemical precursors for the study of O(^{3}P) chemistry in solution.[14] Other methods of oxygen atom formation invariably either require very high energy irradiation or precursors that are themselves involve oxidants (e.g., ozone). To further test and exploit the O(^{3}P) hypothesis,

(1) Photochemistry and Photophysics of Aromatic Sulfoxides. 21. For part 20, see: *J. Am. Chem. Soc.* **2002**, *124*, 2544−2547.

(2) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 217−228.

(3) Gurria, G. M.; Posner, G. H. *J. Org. Chem.* **1973**, *38*, 2419−2420.

(4) Still, I. W. J.; Arora, P. C.; Chauhan, M. S.; Kwan, M.-H.; Thomas, M. T. *Can. J. Chem.* **1976**, *54*, 455−470.

(5) Still, I. W. J. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappaport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons Ltd.: New York, 1988; pp 873−887.

(6) Still, I. W. J.; Cauhan, M. S.; Thomas, M. T. *Tetrahedron Lett.* **1973**, 1311−1314.

(7) Still, I. W. J.; Thomas, M. T. *Tetrahedron Lett.* **1970**, 4225−4228.

(8) El Amoudi, M. S. E. F.; Geneste, P.; Olivé, J.-L. *J. Org. Chem.* **1981**, *46*, 4258−4262.

(9) Jenks, W. S.; Gregory, D. D.; Guo, Y.; Lee, W.; Tetzlaff, T. In *Organic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1997; Vol. 1, pp 1−56.

(10) Kumazoea, K.; Arima, K.; Mataka, S.; Walton, D. J.; Thiemann, T. *J. Chem. Res., Synop.* **2003**, 60−61.

(11) Thiemann, T.; Kumazoe, K.; Arima, K.; Mataka, S. *Kyushu Daigaku Kino Busshitsu Kagaku Kenkyusho Hokoku* **2001**, *15*, 63−71.
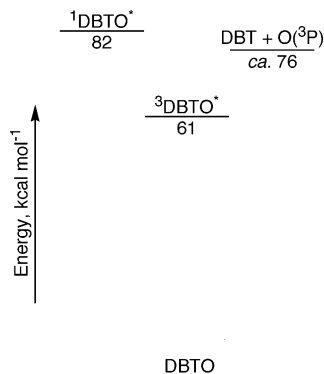
(12) Thiemann, T.; Ohira, D.; Arima, K.; Sawada, T.; Mataka, S.; Marken, F.; Compton, R. G.; Bull, S.; Davies, S. G. *J. Phys. Org. Chem.* **2000**, *13*, 648−653.

(13) Lucien, E.; Greer, A. *J. Org. Chem.* **2001**, *66*, 4576−4579.

(14) Thomas, K. B.; Greer, A. *J. Org. Chem.* **2003**, *68*, 1886−1891.

(15) Wan, Z.; Jenks, W. S. *J. Am. Chem. Soc.* **1995**, *117*, 2667−2668.

(16) Gregory, D. D.; Wan, Z.; Jenks, W. S. *J. Am. Chem. Soc.* **1997**, *119*, 94−102.
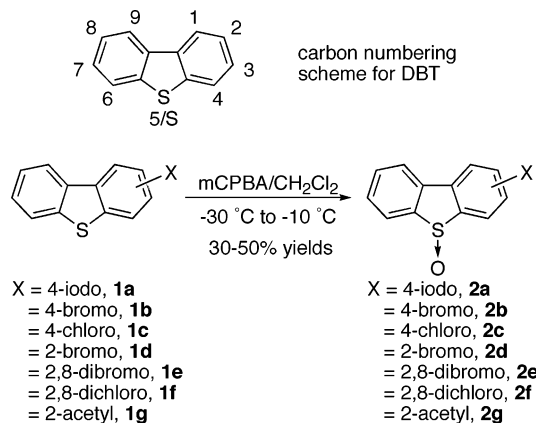
SCHEME 1. Relative Energetics for DBTO Excited States[17] and S−O Dissociation[18]

SCHEME 2. Compound Numbering and Preparation

TABLE 1. Luminescence Quantum Yields

compd	$\Phi_f{}^a$	$\Phi_p{}^b$
DBT	0.09^c	
1a	0.018	
1b	0.045	
1c	0.036	
1e	0.057	
DBTO		0.001
2a		0.065
2b		0.049
2g^d		0.55

^{a} Naphthalene in cyclohexane was used as the actinometer, with excitation at 265 nm.[23] Spectra were obtained in cyclohexane at room temperature. Data were not obtained for **1f**. Otherwise, unlisted compounds did not detectably fluoresce. ^{b} Benzophenone used as an actinometer with excitation at 265 nm.[23] Spectra were obtained at 77 K in EPA frozen organic glass. ^{c} Literature value.[24] ^{d} Measured with 280 nm excitation to avoid a minimum in the absorption spectrum.

however, improved substrates are needed because the chemical quantum yield for **DBTO** photolysis is less than 0.01.[16]

One rationalization of the low quantum yield is that the deoxygenation proceeds by a mechanism in which S−O bond stretching must be accompanied by intersystem crossing at some point before complete bond scission. Such a mechanism is consistent with the energetics of the reaction for **DBTO**, as illustrated in Scheme 1. The fluorescent singlet energy of **DBTO** is about 82 kcal mol^{-1}, and the phosphorescent triplet energy is about 61 kcal mol^{-1}.[17] The S−O bond dissociation energy, forming O(^{3}P), has been estimated to be 75−77 kcal mol^{-1} using computational methods.[18,19] These energetics imply that **DBTO** must be on a path toward scission when isc occurs and not ever reach the phosphorescent triplet, which lacks sufficient energy for S−O dissociation. At the far end of the mechanistic continuum suggested by this idea is the notion that initial scission could result in an ion pair of **DBT**$^{•+}$ and O$^-$, followed by back-electron transfer to the ground state of **DBT** and O(^{3}P).

To the extent that one accepts the unimolecular scission hypothesis and that O(^{3}P) is the reactive intermediate, two goals present themselves for optimization of **DBTO**-like sources of oxygen atoms: (1) a red-shifting of the absorption such that the extinction coefficient is large at more convenient laser lines, such as 355 nm, and (2) an increase in the efficiency of the reaction, so as to generate a higher concentration of O(^{3}P) with a given pulse of light. In this paper, we address a series of experiments aimed mainly at the second of these goals.

One reasonable strategy toward increasing the probability of all isc events is heavy atom substitution. Heavy atom substitution facilitates spin−orbit coupling and, hence, increases the probability (and the absolute rate constants) for both radiative and nonradiative spin-inverting processes.[20,21] Here, we report how adding halogen and acetyl substituents affects the photochemistry and emission of the **DBTO** nucleus.

Results

Compounds. Substituted DBTs (**1a−g**, Scheme 2) were prepared from **DBT** by lithiation and quenching with an electrophile, or by electrophilic aromatic substitution, as detailed in the Supporting Information. Oxidation, using *m*-CPBA at moderately low temperature, provided the corresponding DBTOs (**2a−g**) in satisfactory unoptimized yields.[22]

Luminescence. Fluorescence spectra of the **DBT** derivatives **1a−f** at room temperature in cyclohexane were very similar to that of **DBT**, save for the intensity. Quantum yields are reported in Table 1. The acetyl derivative **1g** did not detectably fluoresce; neither did any of the **DBTO** derivatives **2a−g**.

At 77 K in EPA glass,[25] **DBTO** has a weak phosphorescence.[17] Similar, but somewhat more intense, spectra were obtained from **2a** and **2b**, and approximate quantum yields were measured with respect to benzophe-

(17) Jenks, W. S.; Lee, W.; Shutters, D. *J. Phys. Chem.* **1994**, *98*, 2282−2289.

(18) Jenks, W. S.; Matsunaga, N.; Gordon, M. *J. Org. Chem.* **1996**, *61*, 1275−1283.

(19) This is 10−12 kcal/mol lower than the ordinary S−O BDE of a sulfoxide because of the aromaticity of dibenzothiophene.

(20) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, 1978.

(21) Gilbert, A.; Baggott, P. J. *Essentials of Molecular Photochemistry*; CRC Press: Boca Raton, 1991.

(22) Compound **2b** contained a small amount of an uncharacterized impurity, thought to be an isomer or overhalogenated analogue due to its NMR spectrum, as shown in the Supporting Information. We do not believe this substantially affected any of the reported results.

(23) Eaton, D. F. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Publishers: Boca Raton, FL, 1989; Vol. I, pp 231−239.

(24) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(25) Ethyl ether, pentane, and (ethyl) alcohol, 5:5:2.

TABLE 2. Quantum Yields of Deoxygenation

compd	$\Phi_{deox}{}^a$
2a	$0.0083^b \pm 0.0001^c$
2b	0.0053 ± 0.0001
2c	0.0045 ± 0.0006
2d	0.0056 ± 0.0004
2e	0.0093 ± 0.0009
2f	0.0034 ± 0.0003
2g	~ 0
DBTO	0.0024^d
2b in benzene	0.0220
2b in cyclohexene	0.10
2b in 1:9 cyclohexene/acetonitrile	0.010

a Data were measured by appearance of the sulfide. Solvent is CH_3CN, unless otherwise noted. The actinometer was acetophenone formation from valerophenone.[28] *b* This is the apparent one-photon yield for formation of **1a**, but is a lower limit, due to the efficient photodeiodination of this product. *c* Quoted error bars are standard deviations. *d* Literature value.[16]

none.[23] The spectroscopic triplet energies do not vary widely within the series. These weak spectra are characterized by an onset near 450 nm and are easily obscured by the much more phosphorescent corresponding sulfides, whose spectra have an onset near 400 nm.[26] The acetyl derivative **2g** is highly phosphorescent at 77 K. However, its unstructured spectrum is considerably different, with an onset near 370 nm.[27]

Photolyses. Photoreactions of sulfoxides **2a–g** were carried out in acetonitrile using initial concentrations ranging from 1.5 to 4 mM. The absorption spectra have maxima near 320 nm, so all compounds were excited at that wavelength (± 12 nm) using a Xe-arc lamp filtered through a monochromator. Product analysis was done when the reaction had reached no greater than 10% conversion.

The acetyl derivative **2g** was apparently inert to photolysis, but the other compounds **2a–f** provided the corresponding deoxygenated sulfides. The quantum yields of sulfide formation in acetonitrile were measured, relative to the Type II reaction of valerophenone, and are reported in Table 2.[28] The precision of the results, as reflected in the standard deviations from multiple runs, demonstrates that these differences, though modest, are statistically significant.

In addition to the expected sulfide **1a**, the iodosulfoxide **2a** produced dehalogenated products, i.e., **DBTO** and **DBT**. Such dehalogenations were not observed from any other sulfoxide. Over the course of extensive irradiation of **2a**, the ratio of the products varied with conversion, with **DBT** building up at the expense of the other two, consistent with its formation being via secondary photolysis.

Quantum yield measurement is thus more complicated for **2a**, because of the two primary photochemical reactions: deoxygenation and dehalogenation. Additionally, both secondary reactions lead to **DBT**. However, the quantum yields of the secondary reactions could be measured directly, and the data are presented in Scheme 3.

(26) See, for example, ref 16.

(27) The phosphorescence spectrum of **1g** is considerably more structured and has a blue edge onset near 400 nm.

(28) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506–7512.

SCHEME 3.   Photochemistry and Quantum Yields for Photolysis of 2a in Acetonitrile
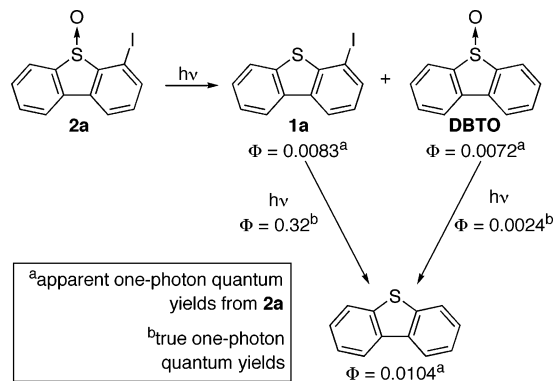
Because the quantum yield of deiodination of **1a** is so much larger than that of any of the other processes, the appearance of **DBT** is approximately linear with time during the early stages of the photolysis, and thus apparent one-photon quantum yields are obtained for the two true primary products (**1a** and **DBTO**) and the secondary product **DBT**. The apparent quantum yields for the primary products are lower than the actual values, which could not be obtained. Because of the efficient conversion of **1a** to **DBT**, it can be concluded that the actual primary quantum yield for dehalogenation of **2a** is substantially greater than that for deoxygenation.

To ensure the validity of the interpretations here, photolyses were carried out through higher conversions. To demonstrate the two-photon pathway to **DBT**, the irradiations were done using different irradiation wavelengths, using RMR-3000 or RMR-3500 fluorescent tubes, centered at about 300 or 350 nm, respectively, in a Rayonet minireactor. The data are shown in Figure 1 with the abscissa normalized to conversion of **2a**, rather than time, for easier comparison of the two. Because of the extended photolysis times required (25 and 37 h, respectively), the photolyses were stopped when none of the starting material remained. Nonetheless, high yields (84% and 91%) of **DBT** were obtained. Because of the relatively high initial concentration of **2a** (ca. 4 mM), some oxidized **DBTO** was also obtained. This product has been previously observed from **DBTO** itself[29] and has been assigned the structure of the corresponding sultine (sufinic ester).

The extinction coefficients for absorption in the 300–320 nm range rank in the order **2a** > **DBTO** > **1a** > **DBT**. Near 350 nm, the order is the same, but the sulfoxides have much greater extinction coefficients than the sulfides. Additionally, some discoloration of the solutions occurs, consistent with the formation of a small quantity of molecular iodine, but no effort was made to document the colored material. The fraction of light absorbed by each compound affects the time course of the product mixture, as indicated in the figure. The essential result, however, is the clear induction period associated with formation of **DBT**, which indicates that it is a secondary photoproduct. Also, the comparable initial yields of **DBTO** and **1a** at low conversion are reflective

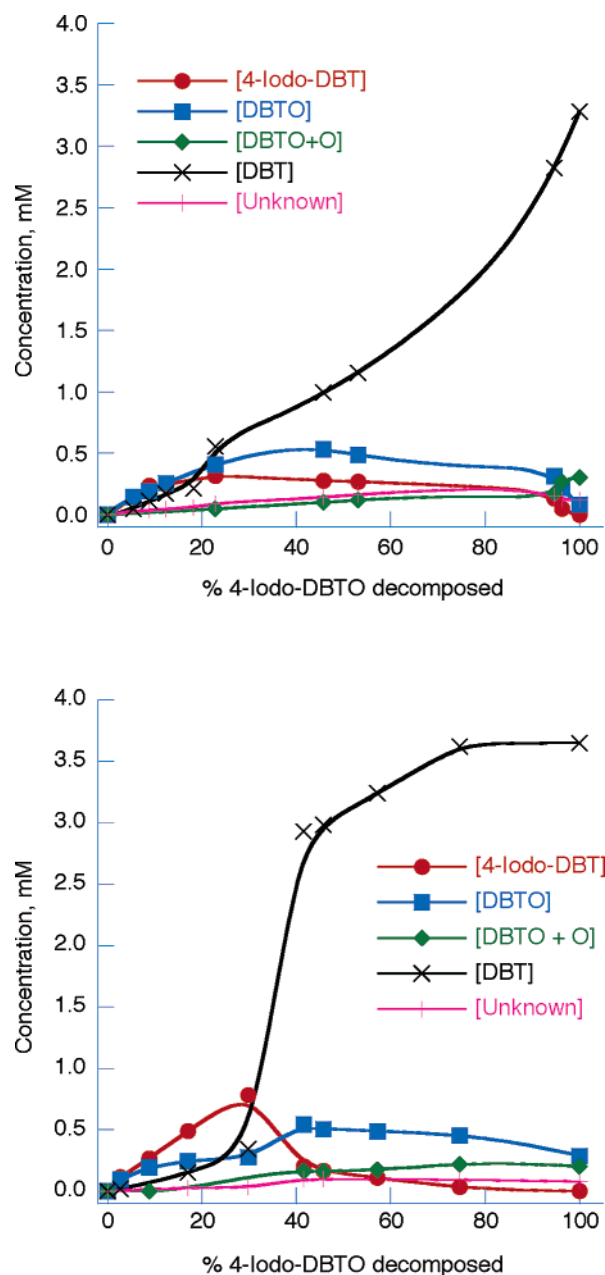(29) Jenks, W. S.; Taylor, L. M.; Guo, Y.; Wan, Z. *Tetrahedron Lett.* **1994**, *35*, 7155–7158.

FIGURE 1. Products observed on photolysis of **2a** in acetonitrile, with initial concentration of 4.0 mM. The abscissas are normalized to percentage decomposition of **2a**. The lines are smooth fits to help draw the eye and of no physical significance. Top: excitation from 300 nm fluorescent tubes. Total time was 1500 min. Bottom: excitation from 350 nm fluorescent tubes. Total time was 2200 min.

of the comparable quantum yields of their formation reported in Scheme 3.

The photochemistry of **2b** was examined in benzene and cyclohexene to verify that the same type of intermediate was formed as in photolysis of **DBTO**. Product studies carried out by the methods previously reported[15,16] showed the same products of solvent oxidation, in nearly identical yield, were obtained using either **DBTO** or **2b**. The major oxidized product from benzene is phenol, while cyclohexene yields both cyclohexenol and cyclohexene oxide in very similar amounts.[15,16] The

quantum yields were also measured and are reported in Table 2.

Discussion

The data presented here support the essential hypotheses used in designing the experiments. The existence of a heavy atom effect is demonstrated by the phosphorescence data, in which the iodosulfoxide and bromosulfoxide have considerably greater quantum yields than **DBTO**. In line with expectations, Cl substitution has little heavy atom effect. Compounds **2c** and **2f** are not phosphorescent, and their deoxygenation quantum yields are only marginally higher than that of **DBTO.** Thus **2c** and **2f** are good control compounds to show that the larger effects in other compounds do not come from a more mundane source, such as desymmetrizing of the chromophore.

Greater phosphorescence yields can result either from greater efficiency in formation of the triplet, or from a greater fraction of triplets undergoing emissive decay, or both. We cannot distinguish among these possibilities. Nonetheless, there is some evidence (see below) for a significant triplet yield for **2a**. In any case, it is quite reasonable to assign the greater phosphorescence quantum yield to heavy-atom-assisted mechanisms. It should also be noted that the fluorescence yields of the substituted DBTs are lower than that of **DBT** itself—consistent with a heavy atom effect—though the value for **1c** is lower than might be expected for a simple trend among the halogenated compounds.

In a previous work,[16] we reported that the use of oxygen, isoprene, or cyclopentadiene as potential triplet quenchers did not lower the quantum yield of **DBTO** deoxygenation. This showed that deoxygenation does not proceed through a typically long-lived triplet state of the sulfoxide. The facts that triplet quenchers do not lower the efficiency of deoxygenation and the triplet excitation energy is below the energy required to carry out S−O scission imply that a higher yield of the spectroscopic triplet would not be inherently favorable for deoxygenation yields. Thus, the classic increase of the intersystem crossing rate in arenes by heavy atoms could be counterproductive. Nonetheless, small but reproducible and significant increases in deoxygenation are obtained with the iodosulfoxide **2a** and the bromosulfoxides **2b**, **2d**, and **2e**, relative to **DBTO** and the chlorinated sulfoxides.

Especially taking into account that it is likely that the triplet yields of **2a**, **2b**, **2d**, and **2e** are higher than that of **DBTO**, we assert that the increased quantum yields for deoxygenation in this series of compounds are consistent with the idea that S−O scission is coupled with intersystem crossing by way of an excited-state surface crossing to a dissociative triplet state. Similar mechanistic assertions have been discussed, for example, in the extensive published work on the photodissociation of aryl halides.[30] Recent computational papers by Liu and co-workers derives explicit potential energy curves for halobenzenes and discuss the surface crossings promoted by halogen-induced spin−orbit coupling in detail.[31,32]

(30) Leading references for this literature are available in refs 31 and 32.
(31) Liu, Y.-J.; Persson, P.; Karlsson, H. O.; Lunnell, S.; Kadi, M.; Karlsson, D.; Davidsson, J. *J. Chem. Phys.* **2004**, *120*, 6502−6509.

Another mechanistic extreme that cannot be eliminated is the photodissociation to an ion pair, presumably **DBT**[•+]/O[•−], followed by back-electron transfer that leads to **DBT** and ground-state O(^{3}P). This back-electron-transfer pathway would naturally compete with simple recombination and thus could also result in a low quantum yield. If the ion pair is born in a singlet state, then heavy atom substitution on the **DBT** moiety might facilitate the back-electron-transfer pathway and raise the quantum yield of O(^{3}P) formation.

The three bromo-substituted compounds were investigated to determine empirically whether a higher quantum yield could be obtained by moving the substituent or adding a second one. From the practical perspective of trying to use these compounds in independent studies of oxygen atom chemistry, the differences are not especially significant, though adding a second bromine does enhance reactivity.

The initial attractiveness of the higher quantum yield for iodinated sulfoxide **2a** is quickly quashed by the complications involved with the dehalogenation reaction. The fact that only it and its corresponding sulfide **1a** undergo the photodehalogenation reaction suggests that this is an orthodox homolysis reaction, which is usually assigned to triplet-state chemistry. (See, for example, refs 33 and 34.) The bond energy for aryl iodides is of the order of 64 kcal mol^{-1}.[33,34] That is just a few kcal mol^{-1} higher than the energy of the spectroscopic triplet of **2a**, probably within reach at room temperature, given the moderate quantum yield. The triplet energies of the **DBT** derivatives is about 70 kcal mol^{-1},[17] which is above the energy required for C−I homolysis and presumably contributes to the higher quantum yield for deiodination of **1a**.

On the other hand, arene−Br bond energies are near 70 kcal mol^{-1}.[33,34] With triplet energies of the order of 60 kcal mol^{-1}, it is not surprising that **2b**, **2d**, and **2e** do not debrominate competitively with deoxygenation. On the other hand, exhaustive photolysis might have led to dehalogenation of the corresponding sulfides, given their higher triplet energies.

The solvent dependence on the quantum yield observed for **2b** is consistent with our previous observations for **DBTO**,[16] though with values all somewhat larger than for the parent. We interpret the solvent dependence in terms of a model suggested in Scheme 4.

On scission, O(^{3}P) is formed in the immediate vicinity of **DBT**. As a result, the reactive intermediate may immediately react with the sulfide to reoxidize it, diffuse away from the sulfide before reacting with anything, or react with solvent before escaping from the cage. To the extent that one solvent reacts with O(^{3}P) faster than another one, the observed quantum yield will be higher. Acetonitrile is not a particularly active substrate for reactions with O(^{3}P).[35] More reactive molecules include halide ions, and those with oxidizable sulfur atoms or

SCHEME 4. Model To Explain Solvent Dependence on Quantum Yields Based on Competition between Reaction with Solvent and DBT
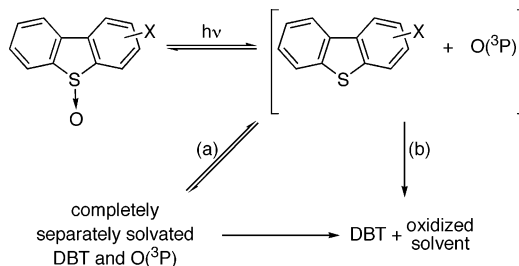
olefins.[16,35] As a result, the observed quantum yields are higher in cyclohexane than acetonitrile.

The strong luminescence and lack of deoxygenation from **2g** can be rationalized in at least two ways. First, the data are consistent with a case in which intersystem crossing to the luminescent triplet is very efficient and in which the photoreactivity of that state is very low. The blue-shifted emission spectrum of **2g**, relative to the other emissive sulfoxides, suggests that the triplet energy may be on par with or just below the S−O bond energy, but the carbonyl group may perturb the nature of the state more than the halogens. The lack of structure in the spectrum suggests it is not a typical localized nπ* state of aromatic ketones such as benzophenone, but assignment beyond that is speculative. There is not a high correlation between phosphorescence yields and reactivity in another prototypical reaction of sulfoxides, photoinduced stereomutation, but the phosphorescence yields for compounds whose racemization have also been studied are all lower than for **2g**.[36−38] A second rationalization, also consistent with all the data, is that the introduction of the acetyl substituent and its attendant electronic influences directly perturbs the coupling between ISC and deoxygenation.

An alternative heavy atom strategy, to be reported separately, is the use of selenoxides instead of sulfoxides in a **DBTO**-like molecule. In this case, the perturbation to the system is inherently greater because of changes in bond strength, bond lengths, aromaticity of the reduced compound, etc. However, the central location of the heavy atom at the key atomic position involved in the S−O (or Se−O) cleavage may turn out to be a more dramatically successful strategy, in terms of producing a high quantum yield O-atom donor.

Conclusions

Halo-substituted dibenzothiophenes show a modest improvement in the quantum yield for deoxygenation, relative to the parent **DBTO**. The trend order of iodo > bromo > chloro ∼ H allows assignment of this to a heavy atom effect. This is consistent with a proposed mechanism of unimolecular S−O scission in which bond stretching is coupled to intersystem crossing, presumably into the T_0 substate. From a quantitative point of view, the effect is smaller than that which would be optimum for

(32) Liu, Y.-J.; Persson, P.; Lunnel, S. *J. Phys. Chem. A* **2004**, *108*, 2339−2345.

(33) Grimshaw, J.; de Silva, A. P. *Chem. Soc. Rev.* **1981**, *10*, 181−203.

(34) Schutt, L.; Bunce, N. J. In *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; Horspool, W. M., Lenci, F., Eds.; CRC Press: Boca Raton, 2004; pp 38-1−38-18.

(35) Bücher, G.; Scaiano, J. C. *J. Phys. Chem.* **1994**, *98*, 12471−12473.

(36) Lee, W.; Jenks, W. S. *J. Org. Chem.* **2001**, *66*, 474−480.

(37) Tsurutani, Y.; Yamashita, T.; Horie, K. *Polymer J.* **1998**, *30*, 11−16.

(38) Tsurutani, Y.; Machida, S.; Horie, K.; Kawashima, Y.; Nakano, H.; Hirao, K. *J. Photochem. Photobiol. A* **1999**, *122*, 161−168.

demanding mechanistic studies of O(^{3}P) solution-phase chemistry that require substantial concentrations of intermediates, such as flash photolysis.

Experimental Section

Photoreactions. All solvents were "spectro grade" or the equivalent and deoxygenated by sparging with argon bubbles for 10 min prior to photolysis. Cyclohexene was refluxed over Na under an Ar atmosphere and distilled immediately before use.

The initial concentrations of all photolyses were in the range of 1.0 to 4.0 mM. Prior to photolysis, the samples were checked for purity using a HP 5890 II gas chromatograph equipped with ZB-5 capillary columns and a flame ionization detector. Dodecane was used as internal standard for all photoreactions. Valerophenone was used as actinometer for quantum yield measurements,[28] and samples were irradiated in 1 cm square cells.

Quantum yields were measured using a 75 W Xe arc lamp fitted to a monochromator set to 320 nm. The full output of the monochromator was absorbed by the samples, whose optical density at the excitation wavelength exceeded 2. Actinometry was repeated frequently to avoid any effect on quantum yield measurement due to any long-term drift in the light flux.

Preliminary photoreactions and some product analysis studies were done using a fan-cooled Rayonet minireactor at room temperature using broadly emitting 300 nm fluorescent tubes. The same reactor was used for the data shown in Figure 1, using both the 300 nm bulbs (RMR-3000) and 350 nm bulbs (RMR-3500).

Emission Spectra. Phosphorescence spectra were recorded at 77 K, as reported previously.[17] The samples were contained in 5 mm Suprasil cylindrical tubes within the Dewar. Fluorescence data were collected at ambient temperature with Ar-flushed samples that had an optical density of about 0.1 at the excitation wavelength, usually 265 nm.

Supporting Information Available: Compound preparation, emission, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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