

Deoxygenation of dibenzothiophene-S-oxide and dibenzoselenophene-Se-oxide: A comparison of direct and sensitized photolysis

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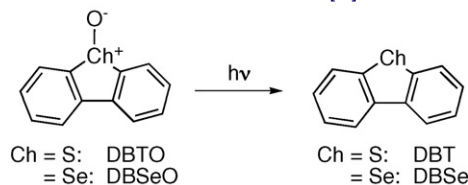
ABSTRACT

Photolysis of dibenzothiophene-S-oxide (DBTO) and dibenzoselenophene-Se-oxide (DBSeO) was examined under direct and sensitized conditions. Quantum yield and solvent oxidation data are used to separate the direct irradiation conditions, plus benzophenone-sensitized and anthraquinone-sensitized irradiation of DBSeO, into one mechanistic class. Acridine-sensitized photolysis of DBSeO and triplet sensitization of DBTO result in deoxygenation, but go by different mechanisms than the direct irradiations. The two sensitized cases that appear mechanistically linked to direct photolysis are ones in which the spectroscopic triplet of DBSeO, which is very likely of comparable energy to the Se–O BDE, is populated by triplet energy transfer.

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1. Introduction

Three primary processes are observed in unimolecular sulfoxide photochemistry: photochemical stereomutation of the S–O bond [1–8], α -cleavage [9–14], and deoxygenation [14–22]. Although the last of these is typically a minor process, it gives high chemical yields some cases, notably derivatives of dibenzothiophene-S-oxide (DBTO). An analogous process, with higher quantum yield, is observed for the selenium analog, dibenzoselenophene-Se-oxide (DBSeO) [23]. Deoxygenation is perhaps the most interesting photochemical reaction of sulfoxides, in that the S–O bond is much stronger than either of the C–S bonds, and the pathway by which loss of the oxygen atom occurs has been a matter of study since the reaction was first discovered in the 1970s [1].



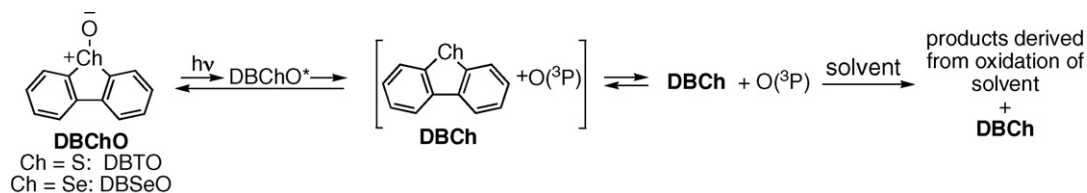
Several mechanisms for photodeoxygenation of sulfoxides have been proposed, but most can now be rejected [17,20]. An early postulated mechanism proceeded by the formation of a dimer: a triplet sulfoxide was trapped by ground state sulfoxide, leading

ultimately to the generation of two sulfide molecules and molecular oxygen. Cross-labeling experiments, low temperature results, and ^{18}O labeling now contradict this. Another proposed mechanism based on O-atom transfer by a sulfinyl radical (RSO^\bullet) subsequent to α -cleavage is energetically infeasible [24]. A mechanism based on hydrogen abstraction by the oxygen atom to form the unstable 9-electron sulfuranyl radical can be eliminated because the reaction proceeds in solvents entirely lacking hydrogen atoms [17].

We proposed that the deoxygenation of certain aromatic sulfoxides on direct photolysis proceeds by unimolecular cleavage of the S–O bond to form $\text{O}(^3\text{P})$ [17]. (We acknowledge that there are additional bimolecular pathways in certain circumstances, such as carbazole or aniline sensitization [25–27].) Perhaps the strongest positive evidence for this mechanism is the pattern of solvent oxidation observed on photolysis of dibenzothiophene-S-oxide (DBTO), as illustrated in Scheme 1 [16,17,20]. Several subsequent investigations have been carried out to test this assertion, and though none has produced direct detection of atomic oxygen, all are consistent with its formation [19,28,29]. Recently, we have also shown that a common intermediate is formed on direct photolysis of DBTO and DBSeO [23]. Additionally, we have directly detected the nitrene formed on photolysis of the *N*-benzoyl analog of DBTO, *N*-benzoyldibenzothiophene sulfilimine [30], and have provided indirect evidence of carbene formation from the S,C-sulfonium ylides derived from dimethylmalonate and DBT [31].

Nonetheless, there is an important aspect of this proposed mechanism of sulfoxide deoxygenation that remains unresolved. As noted previously for DBTO [32,33], there is not sufficient energy in the spectroscopic triplet state of DBTO (ca. 61 kcal/mol) for cleavage

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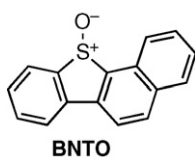


Scheme 1.

(ca. 76 kcal/mol). In our previous work, we simply avoided this issue entirely by carrying out direct irradiation only, and stated that the reaction that produced $\text{O}(^3\text{P})$ could not proceed through the spectroscopic triplet of DBTO. Here, we address the issue of sensitized deoxygenation directly, in large part because it can be an important test of the unimolecular cleavage mechanism. Data showing that triplet sensitization provides the same oxidizing intermediate as direct photolysis would cast very strong doubt on the proposed direct photolysis mechanism. Here we report a study, using literature-established sensitizers, to test just that. To the best of our knowledge, there are no previous reports examining the sensitized photochemistry of selenoxides, and only a few studies have been reported on their direct photolysis [23,34–36].

The earliest studies on deoxygenation were done before the relevant triplet energies were all known [14,15]. Due to the now-known energies of the relevant triplet states, it seems likely that at least many of these sensitized reactions occurred through electron transfer or solvent-mediated chain mechanisms because triplet energy transfer is not plausible. Again, evidence differentiating such a mechanism from that of direct photolysis is required for the $\text{O}(^3\text{P})$ mechanism to be correct.

Recently, de Lucas et al. published a transient absorption study on the benzophenone sensitized photolysis of DBTO [37]. They were able to detect a 370 nm-absorbing transient and ascribed it to a short-lived (143 ns) triplet state of DBTO. Similarly, they observed a somewhat longer-lived transient they associated with the triplet state of the benzannulated analog benzo[*b*]naphtho[2,1-*d*]thiophene-11-oxide (BNTO) originally investigated by Lucien and Greer [20]. In each case, they concurred with previous work that the spectroscopic triplet was not sufficiently energetic for S–O bond scission, but any evidence regarding the similarity or contrast between the direct and sensitized deoxygenation mechanism was indirect.



Even the direct photolysis of DBTO requires an unusual explanation for the apparently spin forbidden reaction of producing $\text{O}(^3\text{P})$ without going through T_1 . We have previously proposed that intersystem crossing from $^1\text{DBTO}^*$ could accompany the bond stretching motion. However, the wavelength dependence reported previously would also be consistent with a mechanism involving a non-spectroscopic T_2 state that lies near the S_1 state in energy [17].

For this study comparing direct and sensitized deoxygenation, we take a two-fold approach. The first is the straightforward measurement of rate constants and quantum yields. The second is a product-based approach in which we characterize the oxidation products formed as a result of the deoxygenation, i.e., what happens to the oxygen atom that is lost from DBTO or DBSeO, regardless of the mechanism. With many solvents (or added reactive traps), oxygenated or otherwise oxidized compounds can be identified. This provides an opportunity for a test against related, but sensitized,

conditions for a common intermediate, since a given intermediate should react with a mixture of traps or a multifunctional trap in a characteristic product ratio (its “oxidation fingerprint”). Grossly different fingerprints for two reaction conditions can be taken to show that different oxidizing species are involved in the reaction conditions being compared.

Details of the sensitization mechanism(s) remain ambiguous, but we now show that direct photolysis is distinct from the sensitized path in most cases. Sensitized deoxygenation of DBSeO also proceeds by a mechanism other than that observed on direct photolysis when sensitizers with a low triplet energy are employed. In certain conditions, the energetics are such that a unimolecular cleavage becomes possible when a sensitizer with a triplet energy greater than the Se–O bond strength is used.

2. Experimental

2.1. Materials

Commercial materials were obtained from Aldrich and Fisher unless specified otherwise. HPLC grade toluene was further purified [38] by washing with cold H_2SO_4 , then once with water, once 5% NaOH, followed with one more wash with water, dried with magnesium sulfate, and distilled from potassium under argon. Benzene and dichloromethane were distilled over CaH_2 under argon. Cyclohexane was purified as described in Perrin and Armarego [38] then dried and distilled from sodium under argon. Peroxides were removed from cyclohexene [38]. Benzophenone was recrystallized from methanol until $\geq 99\%$ pure by GC. All other sensitizers were found to be at least 99% pure by GC as received. Dibenzothiophene-S-oxide and dibenzoselenophene-Se-oxide were prepared by literature methods [23], and further purified by recrystallizations in acetone and dichloromethane, respectively.

2.2. General methods

Photochemical reactions were monitored by GC, HPLC, or both. HPLC separations were done using a Discovery HS C18 reverse phase column and a diode array UV/vis detector. An isocratic solvent mixture of 2:1:1 acetonitrile:methanol:water was used as the eluent. GC analysis was done with a flame ionization detector and 30 m ZB-5 capillary column or a 15 m RTX-1 capillary column. Reported error limits are the standard deviations of multiple runs, and thus reflect the reproducibility of the result, rather than an error limit including any systematic errors.

2.3. Irradiations

Photochemical reactions were irradiated with a 75 W Xe arc lamp focused on a monochromator. Slit widths allowed ± 12 nm linear dispersion from the set wavelength. Samples in a 1 cm square quartz cell were put in a permanently mounted cell holder positioned such that all the exiting light hits the sample cell without further focusing. Photolysis of azoxybenzene was used as an actinometer [39]. Degassing was done by purging with Ar for at least

10 min except as noted. With $n\pi^*$ -triplet sensitizers, this led to modest quantities of oxygenated products in control photolyses that did not have the sulfoxide or selenoxide due to reaction with residual oxygen. The formation of these products is not linear with time, but is rapid initially and tails off as the oxygen is consumed. Other experiments were carried out under freeze–pump–thaw degassing conditions, and the background oxygenation products could be eliminated.

All photolyses were done at ambient temperature. Reactions were typically carried out to about 30% conversion in order to measure the small amounts of minor products. In some cases, it was necessary to carry the reaction to nearly 50% to quantify some products that could only be reliably quantified beginning at about 25% conversion. Both loss of substrate and growth of products were consistently linear with time under these conditions. Control experiments showed that no reaction (either deoxygenation or solvent oxidation) occurred in the dark at temperatures of 40 °C over several hours.

2.4. Spectroscopy

Transient absorption studies were done with a home-built nanosecond transient absorption spectrometer, which has been described previously [13]. Samples were irradiated with the third harmonic of a Nd:YAG (355 nm, 5 ns, 2–25 mJ/pulse, 3 mm beam radius). The spectroscopic detection system included a 75 W Xe arc lamp, a monochromator, an 1P-28 photomultiplier ($R_1 = 50 \Omega$), and a 100 MHz digitizer. Irradiations were carried out in 1 cm square quartz cell. The decay kinetics were typically averaged over 100 laser pulses. Steady state absorption spectra were recorded on a double-beam instrument at room temperature.

3. Results and discussion

Two technical problems made the experiments more difficult than might have been anticipated. They were related to setting up the sensitization reactions ideally (100% light absorption by sensitizer and 100% quenching of sensitizer by substrate) and the reactivity of even small amounts of residual molecular oxygen. Because the sensitizers (benzophenone, anthraquinone and acridine) are known hydrogen abstractors, the inevitable radical chemistry in less than ideal conditions leads to oxygenated products. The problem regarding sensitization could not sensibly be relieved by choice of alternate sensitizers, because the primary goal was to investigate the mechanism of representative known reactions from the literature [14,15]. These limitations make the data also less than ideal; however, important qualitative conclusions can still be drawn.

3.1. Rate constants and quantum yields

DBTO and DBSeO begin to absorb at wavelengths shorter than about 360 nm, with significant extinction coefficients ranging from ~ 6000 to $2000 \text{ M}^{-1} \text{ cm}^{-1}$ from 270 to 320 nm. The selected sensitizers have $n\pi^*$ states and appreciable extinction coefficients over 350 nm. In instances where sensitizer absorption was not intense at wavelengths of at least 350 nm, the sensitizers were used in excess. In all cases, conditions were such that >99% of the light was being absorbed by the sensitizer.

Quenching rate constants and sensitizer triplet lifetimes were measured to attempt to set up conditions where all or nearly all the sensitizer would be quenched by DBTO or DBSeO. These measurements were made by standard transient absorption techniques, using the well-known triplet absorption spectra of the sensitizers [40]. The results are given in Table 1 and typical data are shown in Figs. 1 and 2. de Lucas et al. reported a rate constant

Table 1
Rate constants for quenching of sensitizers by DBTO and DBSeO

Sensitizer	Quencher	Solvent	$k_q (\text{M}^{-1} \text{s}^{-1})$	$1/\tau_0 (\text{s}^{-1})$
Acridine	DBTO	Acetonitrile	$<10^5$	4.3×10^5
	DBTO	CH_2Cl_2	$<10^5$	2.7×10^4
	DBTO	Toluene	$(4.7 \pm 0.6) \times 10^5$	5.0×10^3
Anthraquinone	DBTO	CH_2Cl_2	$(5.7 \pm 1.0) \times 10^8$	4.2×10^6
Benzophenone	DBTO	Acetone	$(4.2 \pm 0.6) \times 10^9$	1.6×10^5
	DBTO	CH_2Cl_2	$(2.8 \pm 0.2) \times 10^9$	5.4×10^5
	DBTO	Toluene	$(4.4 \pm 0.2) \times 10^9$	3.8×10^5
Acridine	DBSeO	CH_2Cl_2	$<10^5$	4.30×10^5
Anthraquinone	DBSeO	CH_2Cl_2	$(1 \pm 0.2) \times 10^9$	4.20×10^6
Benzophenone	DBSeO	CH_2Cl_2	$(4.8 \pm 0.3) \times 10^9$	5.35×10^5

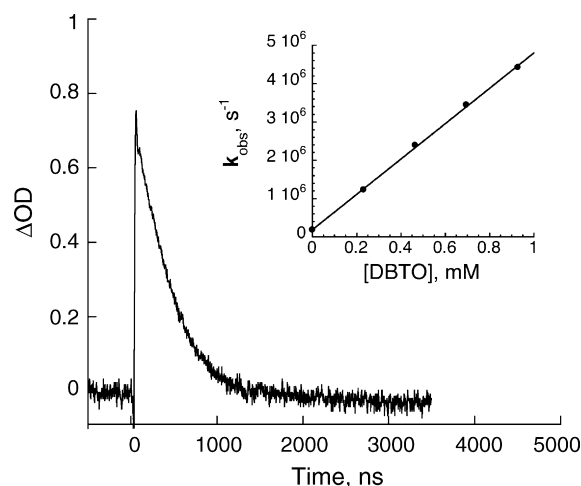


Fig. 1. Kinetic trace at 530 nm acquired after 355 nm excitation of $9 \times 10^{-3} \text{ M}$ benzophenone and $0.5 \times 10^{-3} \text{ M}$ DBTO in acetone. (Inset) The rate of decay or the 530 nm transient as a function of the concentration of DBTO.

of $9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the quenching of benzophenone by DBTO in acetonitrile [37], in keeping with the current data.

The data in Table 1, in combination with Eq. (1), show that in the range of several mM initial concentration, DBTO and DBSeO both quench a very large fraction of benzophenone, but that a small

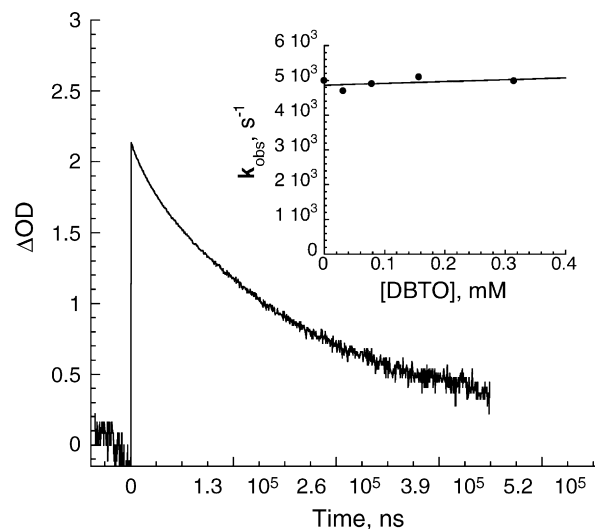


Fig. 2. Kinetic trace at 440 nm acquired after 355 nm excitation of $0.2 \times 10^{-4} \text{ M}$ acridine and $3 \times 10^{-4} \text{ M}$ DBTO in toluene. (Inset) The rate of decay or the 440 nm transient as a function of the concentration of DBTO.

Table 2
Quantum yields for loss of oxide from sensitized DBTO or DBSeO photolyses^a

Entry	Sensitizer	[Sens] (mM)	λ_{ex} (nm)	Φ_{obs}	Φ_{T}	Φ_{sens}	Φ_{rxn}
1	DBTO ^a	None	313	0.0118 ± 0.0013	–	–	0.012
2	DBTO	Acridine	357	0.0048 ± 0.0004	0.5 ^b	0.16	0.061
3	DBTO	Anthraquinone	355	0.0313 ± 0.0016	0.9	0.58	0.060
4	DBTO	Benzophenone	365	0.0074 ± 0.0005	1.0	0.92	0.0080
5	DBTO	<i>N</i> -Methylcarbazole	25	0.0152 ± 0.0016	0.4	–	–
6	DBSeO ^a	None	320	0.301 ± 0.056	–	–	0.30
7	DBSeO	Acridine	357	0.048 ± 0.011	0.5	^c	^c
8	DBSeO	Anthraquinone	355	0.709 ± 0.052	0.9	0.704	1.2
9	DBSeO	Benzophenone	80–100	0.326 ± 0.021	1.0	0.900	0.36

^a Solutions of DBTO and DBSeO were originally 0.4–5 mM and flushed with Ar to remove air. Solvent for DBTO was toluene. Due to solubility issues, the solvent for DBSeO was toluene with 4% chloroform as a co-solvent. Under these conditions all of the light is absorbed by the sensitizer.

^b Ref. [40] or [44].

^c Unable to calculate due to low k_q .

amount of sensitizer remains unquenched (Table 2).

$$\Phi_{\text{sens}} = \frac{k_q[Q]}{k_q[Q] + \tau_0^{-1}} \quad (1)$$

Increasing the concentration of DBTO or DBSeO too far means increasing the small fraction of direct irradiation and is undesirable for straightforward data interpretation [41]. For the sensitizers other than benzophenone, this is more severe: smaller fractions of the sensitizer are quenched at reasonable DBTO/DBSeO concentrations. This affects both quantum yield measurements and product distributions (vide infra).

In previous work, we have shown that the triplet energy of DBTO, as judged by the blue edge shoulder of phosphorescence, varies between 60 and 65 kcal/mol depending on the polarity of the solvent [32]. We were not successful in obtaining a phosphorescence spectrum for DBSeO at 77 K in organic glasses [23,42]. However, based on the similarity of the triplet energy of DBT and DBSe, and the fact that the oxidation tends to remove the S or Se as a part of the active chromophore, we presume that the “spectroscopic” triplet energy of DBSeO is about the same as that of DBTO, i.e., between 60 and 65 kcal/mol.

Triplet energy transfer is plausible as a quenching mechanism for benzophenone ($E_{\text{T}} \sim 69$ kcal/mol) and anthraquinone ($E_{\text{T}} \sim 63$ kcal/mol), but not for acridine ($E_{\text{T}} \sim 45$ kcal/mol) [40]. The rapid quenching of benzophenone (Fig. 1) and somewhat slower quenching of anthraquinone are consistent with exothermic and near-thermoneutral energy transfer. The low rate constant for acridine quenching by DBTO or DBSeO (e.g., Fig. 2) is consistent with a slower mechanism, such as, for example, endothermic electron transfer. We have previously concluded that DBTO undergoes electron transfer reactivity with *N*-methylcarbazole [26].

Table 3
Quantum yields for formation of sulfide or selenide from sensitized DBTO or DBSeO photolyses^a

Entry	Sensitizer	[Sens] (mM)	λ_{ex} (nm)	$\Phi_{\text{oxide}}^{\text{b}}$	$\Phi_{\text{obs}}^{\text{c}}$	Φ_{T}	Φ_{sens}	Φ_{rxn}
1	DBTO ^a	None	313	0.0118 ± 0.0013	0.0046 ± 0.0007	–	–	0.0046
2	DBTO	Acridine	357	0.0048 ± 0.0004	0.0035 ± 0.0003	0.5 ^d	0.158	0.0443
3	DBTO	Anthraquinone	355	0.0313 ± 0.0016	0.0260 ± 0.0021	0.9	0.575	0.0502
4	DBTO	Benzophenone	365	0.0074 ± 0.0005	0.0070 ± 0.0010	1.0	0.920	0.0076
5	DBTO	<i>N</i> -Methylcarbazole	25	0.0152 ± 0.0016	0.0116 ± 0.0001	0.4	–	–
6	DBSeO ^a	None	320	0.301 ± 0.056	0.236 ± 0.025	–	–	0.236
7	DBSeO	Acridine	357	0.048 ± 0.011	0.027 ± 0.002	0.5	^e	^e
8	DBSeO	Anthraquinone	355	0.709 ± 0.052	0.531 ± 0.037	0.9	0.704	0.838
9	DBSeO	Benzophenone	80–100	0.326 ± 0.021	0.207 ± 0.009	1.0	0.900	0.230

^a Solutions of DBTO and DBSeO were originally 0.4–5 mM and flushed with Ar to remove air. Solvent for DBTO was toluene. The solvent for DBSeO was toluene with 4% chloroform as a co-solvent. All of the light is absorbed by the sensitizer.

^b Observed quantum yield for loss of DBTO or DBSeO, respectively.

^c Observed quantum yield for formation of DBT or DBSe, respectively.

^d Ref. [40] or [44].

^e Unable to calculate due to low k_q .

Tables 2 and 3 give the observed quantum yields for loss of DBTO/DBSeO and formation of DBT/DBSe, respectively, along with the conditions used for the measurements [43]. Given the quenching rate constants, the inherent quantum yield for the sensitized reaction can be calculated according to Eq. (2), where Eq. (1) is used to estimate Φ_{sens} . We used $\Phi_{\text{triplet}} = 1, 0.9, 0.5,$ and 0.44 for benzophenone, anthraquinone, acridine, and *N*-methylcarbazole, respectively [40,44].

$$\Phi_{\text{obs}} = \Phi_{\text{triplet}} \Phi_{\text{sens}} \Phi_{\text{rxn}} \quad (2)$$

Eqs. (1) and (2) are used under the assumption that the reaction is based on a simple sensitization/quenching scheme. They thus have an upper limit for Φ_{rxn} of 1. The observed value of 1.2 for anthraquinone and DBSeO (entry 8; Table 2) is probably within experimental error of that limit.

We cannot calculate a value for acridine because the quenching rate constant is too low. This is *prima facie* evidence that at least acridine-sensitized DBSeO photolysis does not go by any simple sensitized mechanism. The most likely explanation is radical-mediated chemistry, probably initiated by hydrogen abstraction by the acridine.

Notable also is that the Φ_{rxn} value is similar for direct irradiation (entry 6) and benzophenone-sensitized chemistry (entry 9), with the latter higher by about 20%. Since the benzophenone-sensitized data presumably reflect the fate of all of the ³DBSeO that is formed, the somewhat smaller, but comparable, value on direct irradiation is consistent with the two processes having the same general mechanism (i.e., through ³DBSeO), as long as the quantum yield for ³DBSeO formation on direct irradiation is in the range of 0.7–0.8.

Table 4
Product yields of photolysis of DBTO and DBSeO in toluene^a

Entry	Sensitizer	[Sens] (mM)	λ_{ex} (nm)	DBT (%) ^b	Benzyl oxidations ^c		Cressols ^c		Benzyl:cresol	
					PhCHO	BnOH	<i>o</i>	<i>m</i> and <i>p</i> ^d		
1	DBTO ^a	None	–	313	55 ± 11	17 ± 4	13 ± 4	26 ± 5	22 ± 5	1:1.6
2	DBTO	Acridine	11	357	75 ± 8	45 ± 5	26 ± 5	6.5 ± 0.5	–	–
3	DBTO	Anthraquinone	10	355	83 ± 8	9.6 ± 2.2	8.9 ± 0.6	3.5 ± 0.4	1.8 ± 0.4	3.5:1
4	DBTO	Benzophenone	100	365	94 ± 9	30 ± 3	27 ± 3	3.4 ± 0.5	3.6 ± 0.7	8.1:1
5	DBTO	<i>N</i> -Methylcarbazole	25	350	77 ± 8	3.2 ± 0.8	3.4 ± 0.8	3.3 ± 0.1	1.1 ± 0.2	1.5:1
6	DBSeO ^a	None	–	320	80 ± 7.6	6.7 ± 1.6	–	12 ± 0.5	5.2 ± 0.4	1:2.6
7	DBSeO	Acridine	11	357	58 ± 10	23 ± 3	3.9 ± 1.5	7.0 ± 0.7	2.8 ± 0.5	2.7:1
8	DBSeO	Anthraquinone	10	355	75 ± 4	17 ± 1.5	7.7 ± 1.5	5.8 ± 1.5	3.3 ± 1.1	2.7:1
9	DBSeO	Benzophenone	80–100	365	64 ± 1.3	6.0 ± 1.9	1.2 ± 2.6	12 ± 2.3	7.6 ± 0.4	1:2.7

^a Solutions of DBTO were originally 1–5 mM and flushed with Ar to remove O₂. Solutions of DBSeO were originally 0.4–2 mM and flushed with Ar to remove O₂. Chloroform (4%) was added as a co-solvent to increase DBSeO solubility.

^b Yield, relative to loss of DBTO or DBSeO.

^c Yield relative to formation of DBT or DBSe.

^d Measured as one peak.

The Φ_{rxn} quantum yields recorded for acridine or anthraquinone and DBTO (entries 2 and 3 in Table 2) are essentially identical, but almost an order of magnitude larger than that when using benzophenone (entry 4). As will become clear below, we conclude that the mechanism for deoxygenation of DBTO under direct irradiation is different than that under sensitized conditions, regardless of which sensitizer is used. (However, this does not positively demonstrate that all of the sensitized reactions follow the same mechanism.) Assuming the mechanism for DBTO deoxygenation does not directly involve ³DBTO – as concluded for entry 7 with DBSeO – there is no particular reason that these then-meaningless Φ_{rxn} values should coincide for various sensitizers. We thus do not derive any particular meaning from their difference.

3.2. Oxidation fingerprint experiments

In our original report on DBSeO photochemistry, we demonstrated that DBSeO and DBTO gave very similar “fingerprints” on oxidation of toluene, with a predominance of cresols being formed over products from benzyl oxidation (benzyl alcohol and benzaldehyde) [23].

Toluene was chosen as an initial solvent and trap, due to the mix of easily identifiable products: the three possible cresols, benzyl alcohol, and its over-oxidation product, benzaldehyde. *m*-Cresol and *p*-cresol were quantified as a single peak by GC because of the difficulty of their separation. Table 4 lists the percent yields of sulfide (DBT) relative to loss of sulfoxide (DBTO) in entries 1–5. The yields of oxidized products, relative to the formation of DBT, are given in the other columns (Scheme 2).

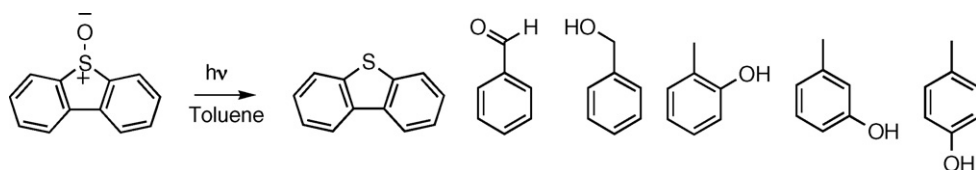
Analogous data are given for the DBSeO reaction in entries 6–9. It was determined that addition of a small amount of chloroform (4 vol.%) enhanced the solubility of DBSeO in toluene and was necessary for homogenous solutions. Control experiments with DBTO showed that addition of this amount of chloroform to the toluene did not affect the data.

Fairly large error bars are associated with the data for benzyl alcohol and benzaldehyde. Empirical experimentation with deoxygenation techniques indicated that the *sum* of these two products

was much more reproducible than either individual number, and that the “overoxidation” of the benzyl alcohol to benzaldehyde was probably correlated with residual oxygen in solution. Further experiments using the more rigorous freeze-pump-thaw method for deoxygenation of DBSeO under direct, benzophenone-sensitized, and anthraquinone-sensitized conditions showed that benzaldehyde could be eliminated from the product mixture. FPT degassing was not used in most experiments, though, because only a single time point can be taken from the sample.

Because of the low concentrations of oxygenated species being detected in the measurements and the potential for their formation by reactions between the sensitizer, solvent, and residual O₂, appropriate control experiments were run. Solutions were prepared without DBTO or DBSeO, but otherwise identically to those of the ordinary runs, i.e., they contained the sensitizers at the appropriate concentrations and were deoxygenated the same way. The following key results were obtained: (1) in no case was any cresol detected; (2) though small amounts of PhCH₂OH and PhCHO were detected, in no case did those quantities exceed one-tenth that observed in the measurements that contained sensitizer and DBTO that were photolyzed for the same amount of time, particularly for higher conversions. An analogous conclusion holds for DBSeO [45].

However, entry 8 in Tables 2–4 merits special discussion. Photolysis of anthraquinone in the absence of DBSeO with Ar-flushing deoxygenation does lead to benzyl oxidation products that are significant to the concentrations reported in the table. (Again, cresols were not observed.) With the measurements reported in these tables, only about 10% of the anthraquinone is actually quenched, with anthraquinone absorbing >99% of the light. Because of solubility limitations, a significantly higher fraction of anthraquinone quenching could not be achieved. Thus, most of the anthraquinone “control chemistry” is still occurring under these experimental conditions, and most of the benzyl oxidation products in entry 8 comes from this direct interaction between anthraquinone and solvent. In contrast, under FPT degassing, the oxidation fingerprint for anthraquinone-sensitized DBSeO photolysis is dominated by cresol formation, quite similar to direct or DBSeO or benzophenone-sensitized photolysis of DBSeO.



Scheme 2.

Table 5
Product yields from photolysis of DBTO in dichloromethane and 20% 3:1 benzene:cyclohexane^a

Entry	Sensitizer	[Sens] (mM)	λ_{ex} (nm)	Sulfide/selenide (%) ^b	Cyclohexanol (%) ^c	Phenol (%) ^c
1	DBTO	None	320	49 ± 4	32 ± 5	10 ± 0.1
2	DBTO	Benzophenone	365	95 ± 1	20 ± 5	–
3	DBSeO	None	320	61 ± 10	3.8 ± 0.3	2.4 ± 0.5
4	DBSeO	Benzophenone	365	86 ± 9	14 ± 3	3.0 ± 0.6

^a Initial concentrations of DBTO or DBSeO were 1–2 mM and flushed with Ar to remove oxygen.

^b Percent yield, relative to loss of DBTO or DBSeO.

^c Percent yield, relative to formation of DBT or DBSe.

Table 4 immediately draws attention to the difference between direct photolysis and the other conditions by presenting the ratio of benzyl oxidation products (benzyl alcohol and benzaldehyde) to cresols. Even allowing for relatively large uncertainties in the data due to the low concentrations being measured, the preponderance of cresol products over benzyl oxidation for direct irradiation is in direct contrast to all the other cases. Our current data give slightly different ratios for direct irradiation of both DBTO and DBSeO (entries 1 and 6) than our previous report in such a way as to make the data for the two compounds look less similar. (The ratios were 2.0 and 2.8, rather than 1.6 and 2.6, for DBTO and DBSeO, respectively [23].) We attribute this to the difficulties with residual O₂. Nonetheless, the salient result remains that direct irradiation of the two compounds leads to the cresols as the major product, with a substantial minor pathway giving benzyl alcohol and benzaldehyde. In contrast, all of the sensitized DBTO reactions (entries 2–5) lead to large majorities of benzyl oxidations. Among the DBSeO reactions, the benzophenone sensitization (entry 9) stands out as being much more like the direct irradiations than the other sensitized reactions (entries 7 and 8), in addition to anthraquinone-sensitized DBSeO photolysis when FPT is used.

An alternative second trap was pursued. Originally, we examined cyclohexene, which produces the epoxide and cyclohexenol with DBTO [16,17], but this trap was fraught with reproducibility-related difficulties when the sensitizers that could also accomplish hydrogen abstraction were used.

Ultimately a 3:1 (v/v) mixture of benzene and cyclohexane was used, based on selectivity results reported previously [17]. Cyclohexanol and phenol were used as the fingerprint products. To best accommodate solubility, this mixture was used as a 20% cosolvent with 80% dichloromethane. Results for direct and benzophenone-sensitized photolysis are given in Table 5.

Despite the poor mass balances reflected in Table 5, particularly for DBSeO, we believe some analysis can still be made. An approximately 3:1 ratio of cyclohexenol:phenol is achieved by direct photolysis of DBTO. The observed ratio for DBSeO is somewhat lower (entry 3, direct) or higher (entry 4, benzophenone-sensitized). However, it should also be noted that the absolute yields of the oxygenated products are low in this solvent mixture, particularly for DBSeO. They are thus subject to a larger proportion of systematic error due to the presence of residual oxygen and radical chemistry. Nonetheless, we suggest these imperfect data still show that entries 1 and 2 are mechanistically distinct from one another. Conclusions regarding DBSeO must be considerably more tentative, but that entries 3 and 4 produce similar results is consistent with the toluene data and the hypothesis that benzophenone-sensitized deoxygenation of DBSeO may go through the same mechanism as direct irradiation of DBSeO.

3.3. Differentiating mechanisms

As discussed previously, we have estimated that the T₁ energy of DBTO is between 60 and 65 kcal/mol, depending on the solvent;

DBSeO should be very similar [32]. However, while the S–O BDE of DBTO is about 76 kcal/mol, we have estimated that the Se–O BDE for DBSeO is only about 64 kcal/mol [46]. Thus, it is at least plausible that DBSeO may undergo dissociation to DBSe and O(³P) from the T₁ state of DBSeO. On the other hand, T₁ simply is not energetic enough for S–O dissociation in DBTO.

It is thus satisfying that, while the data presented in this paper are less than perfect, in each case, they can be broken into two qualitative groups. In the first group reside data from direct photolysis of both precursors, benzophenone-sensitized photolysis of DBSeO, and anthraquinone-sensitized photolysis of DBSeO (if done with FPT degassing). The other group, consisting of the rest of the condition sets, is more diverse in terms of its results, but all of them contrast to the first group. We conclude that the two groups do not share a common intermediate or mechanistic path.

4. Conclusions

The results reported here place the chemistry of direct irradiation of DBTO, direct irradiation of DBSeO, and either benzophenone- or anthraquinone-sensitized photolysis of DBSeO into a single group of reactions with regard to oxidative selectivity. Though it must be acknowledged that the data are not perfect, this is a sensible grouping. Direct irradiation of DBTO and DBSeO both produce O(³P), we have argued. The two sensitized cases in this group are those where energy transfer to form triplet DBSeO is plausible, and we estimate that ³DBSeO probably has enough energy for unimolecular Se–O scission.

In contrast, the other sensitizing combinations lead to cases that cannot directly form O(³P). Formation of triplet DBTO (from benzophenone and probably anthraquinone) may result in deoxygenation, but not by the same mechanism as direct irradiation. Sensitization of either substrate with acridine simply cannot result in triplet formation. Thus, it is no surprise that the oxidation patterns of this second group differ from that of the first. These experiments do not shed significant light on the mechanism(s) of the sensitized deoxygenations, but they are set apart from the conditions of the former group.

Thus, we again conclude that the data here add to the circumstantial evidence that photolysis of DBTO or DBSeO produces atomic oxygen.

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- [42] A careful reading of reference 32 will reveal that a majority of this type of sulfoxides does not produce useful phosphorescence data, i.e., DBTO was one of the few exceptions. We routinely examine new sulfoxides or selenoxides for phosphorescence at 77 K, but are not surprised when a useful spectrum is not obtained.
- [43] The values reported here were remeasured for this work, as we have done for each paper in the series that addresses this reaction. We find that measured quantum yields are quite reproducible when measured repeatedly over a short time span for a project such as the current one. However, some variation from previously reported values for DBTO photolysis is common, and not unexpected due to the fairly severe dependence on wavelength, solvent-dependence, and inherently low value.
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