

Photooxidation of Dibenzothiophene and 4,6-Dimethyldibenzothiophene Sensitized by *N*-Methylquinolinium Tetrafluoroborate: Mechanism and Intermediates Investigation

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Photooxidation of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) sensitized by *N*-methylquinolinium tetrafluoroborate ($\text{NMQ}^+\text{BF}_4^-$) has been investigated in O_2 -saturated acetonitrile solutions. Nearly 100% oxidation of DBT and DMDBT was observed, and the oxidized products are predominantly composed of sulfoxides and sulfones, which are formed via photoinduced electron transfer (ET). Such ET processes were studied with fluorescence quenching of NMQ^+ , time-resolved transient absorption measurement, and ESR experiments. The fluorescence of NMQ^+ is efficiently quenched by DBT and DMDBT via diffusion-controlled processes, with bimolecular quenching constants of $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for DBT and $2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for DMDBT. The electron-transfer nature of the quenching is evidenced by the transient absorption measurement of the neutral radical NMQ^\bullet , which is formed by electron transfer from the substrates (DBT or DMDBT) to the excited singlet state of NMQ^+ . The ESR spectra of the superoxide radical anion ($\text{O}_2^{\bullet-}$) trapped by 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) in the photooxygenation of DBT and DMDBT as well as their sulfoxides manifest that O_2 traps an electron from NMQ^\bullet to form $\text{O}_2^{\bullet-}$. The fact that the formation of sulfoxides and sulfones is greatly suppressed in the presence of benzoquinone (BQ), an efficient electron trap for NMQ^\bullet and $\text{O}_2^{\bullet-}$, further indicates an ET process in the photooxidation of DBT and DMDBT. As inferred from the control experiments, the role of singlet oxygen ($^1\text{O}_2$) in the photooxidation is negligible. The intermediates responsible for the formation of sulfoxides and sulfones have been examined in detail.

Introduction

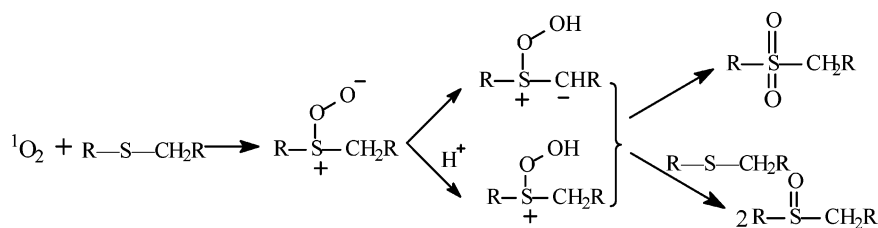
Photooxidation of sulfides has attracted considerable interest in view of the practical application in the synthesis, desulfurization of light oil, and biological implications.^{1–7} The $^1\text{O}_2$ oxygenation of sulfides has been extensively studied since Schenck and Krauch's report in 1962,⁸ and presently it is generally accepted that persulfoxide ($\text{R}_2\text{S}^+-\text{OO}^- \leftrightarrow \text{R}_2\text{S}^\bullet-\text{OO}^\bullet$) is the first intermediate, followed by conversion to the second intermediate, *S*-hydroperoxysulfonium ylide, through the intramolecular α -proton abstraction or intermolecular proton transfer (Scheme 1).^{9–11} Photooxidation via electron transfer (ET) sensitization is another main photooxidation mechanism, which possesses particular advantages. The photoinduced electron transfer can be controlled by choosing photosensitizers with different one-electron redox potentials.¹² However, less information is currently available for the photooxidation of sulfides via photoinduced ET mechanism. Based on the trapping experiments and theoretical calculations, Baciocchi et al.¹³ have recently found that only sulfoxide is produced in an ET mediated photooxygenation, and a thiadioxirane intermediate is responsible for the single product formation (Scheme 2). This is different from the case of the $^1\text{O}_2$ photooxygenation where both sulfoxide and sulfone were formed and the thiadioxirane

intermediate was deemed impossible.^{14,15} However, for either ET or $^1\text{O}_2$ photooxidation, the previous work has mainly focused on the substrates of alkyl alkyl sulfide or aryl alkyl sulfide with α -H. Little investigation has been carried out on such aromatic sulfides as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) which have no α -H. The absence of α -H in DBT and DMDBT suggests no possibility of forming the *S*-hydroperoxysulfonium ylide intermediate in the photooxidation in aprotic solutions, whereas the same intermediate can be formed in the photooxygenation of sulfides with α -H. Studies of photooxidation of DBT and DMDBT could therefore offer us a comprehensive understanding of the photoinduced ET reactions of sulfides.

DBT and DMDBT, the main sulfur-containing compounds in diesel oil, are the most difficult to remove by the current method of hydrodesulfurization (HDS).¹⁶ Operation at high temperatures and pressures is inevitably required to remove these refractory sulfur molecules and obtain the ultra-deep desulfurization of diesel fuels. However, this brings many problems such as high operating cost and an increase in the hydrogen consumption.^{16d} Exploration of some alternative desulfurization processes thus becomes one of the major goals of the current research. It has been known that DBT and DMDBT can be readily removed from diesel oil by liquid–liquid extraction after they are oxidized to sulfuroxides and/or sulfones, which have greater polarity than the corresponding sulfides.¹⁷ While the

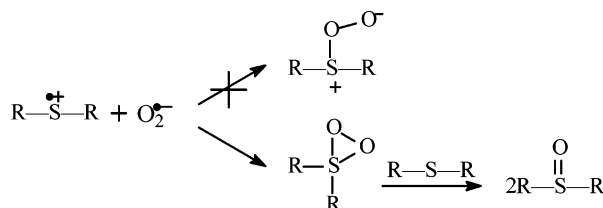
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SCHEME 1



oxidation has been successfully carried out with H_2O_2 or other non-hydrogen peroxide systems, molecular oxygen mediated photooxidation may have greater potential practical value for environmental and economic respects. In this work, the photooxidation of DBT and DMDBT has been investigated in the oxygen-saturated acetonitrile solution by using NMQ^+ as the sensitizer. Complete oxidation of DBT and DMDBT was observed, and both sulfoxide and sulfone were detected as the oxidized products. Moreover, sulfones are from the photooxidation of sulfoxides. The transient absorption spectra and the electron spin resonance (ESR) spectra combined with the trapping experiments imply that the formation of sulfoxides and sulfones is due to the photoinduced ET mechanism, while the $^1\text{O}_2$ simultaneously produced by the excited NMQ^{+13} has negligible contribution to the photooxidation.

SCHEME 2



Experimental Section

Materials. Dibenzothiophene (DBT) and 4,6-dimethylbenzothiophene (DMDBT) were purchased from Aldrich and were used as received. *N*-methylquinolinium tetrafluoroborate ($\text{NMQ}^+\text{BF}_4^-$) was synthesized according to the literature procedure^{18,19} with the following modifications. Ethyl acetate instead of diethyl ether was used as reaction solvent and the obtained product was purified by exhaustive solid-liquid extraction utilizing the ethyl acetate through micro-Soxhlet equipment. The reagent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), used as a spin trap, was purchased from Sigma Chemical Co. Ethyl acetate, acetonitrile, quinoline, Eosin, and *p*-benzoquinone (BQ) were of analytical reagent-grade and were used without further purification.

General Photooxidation Procedure. The photooxidation of DBT (5.4×10^{-3} M) and DMDBT (4.6×10^{-3} M) sensitized by NMQ^+ (5% mol) was carried out in an oxygen-saturated acetonitrile solution contained in a cylindrical Pyrex flask (allowing for 310 nm cutoff irradiation). A 100-W Hg lamp (TOSHIBA Lighting and Technology Corporation, Japan) was used as the light source. Oxidation products were detected by an HPLC technique (Dionex P580 pump and UVD340S diode array detector) using an Intersil ODS-3C-18 inverted-phase column. The eluent gradient was regulated by water and acetonitrile. For the photooxidation products of DBT, the acetonitrile gradient ranged from 40% to 80% in the first 20 min and from 80% to 100% in the next 10 min. For the photooxidation products of DMDBT, the acetonitrile gradient

ranged from 40% to 80% in the first 20 min and from 80% to 100% in the next 1 min and held at 100% in the last 9 min. The products were identified by mass spectra (on Finnigan Trace DSQ instrument) and infrared (IR) spectra (on a Digilab FTS3500 Fourier Transfer Infrared spectrometer).

Laser Flash Photolysis. The measurements of transient absorption spectra in the photooxidation of DBT or DMDBT with NMQ^+ in acetonitrile were performed with use of a nanosecond laser flash photolysis system. The acetonitrile solution was purged with argon or oxygen gas for 20 min prior to the measurement. Then the solution was excited by a Nd:YAG laser (Continuum, surelite II, third harmonic) at 355 nm (pulse width ca. 7 ns and energy <3 mJ per pulse). The transient spectra were obtained by a point-to-point technique, monitoring the change of absorbance (ΔV) after the laser flash at intervals of 10 nm over the spectral range 400–850 nm. All measurements were performed at about 25 °C.

ESR Measurements. Electron spin resonance (ESR) signals of radicals trapped by DMPO were obtained on a Bruker model ESP300E electron paramagnetic resonance spectrometer equipped with a Quanta-Ray Nd:YAG laser system as the irradiation light source ($\lambda = 355$ nm) at ambient temperature. The settings were center field 3480.00 G, microwave frequency 9.79 GHz and power 5.05 mW.

Fluorescence Quenching. The fluorescence lifetimes of NMQ^+ (8.6×10^{-6} M) in the absence and presence of DBT at various concentrations (2.7×10^{-5} to 4.3×10^{-4} M) or DMDBT (2.4×10^{-5} to 2.4×10^{-4} M) were determined by single photon counting on a Horiba NAES-1100 time-resolved spectrofluorophotometer. The excitation wavelength was 325 nm and the emission wavelength was 400 nm. A linear Stern–Volmer relationship

$$\tau_0/\tau = 1 + K_q[D]$$

was obtained for the lifetime (τ) of NMQ^+ as a function of the concentration of the quencher [D]. The quenching rate constants $k_q (=K_q\tau_0^{-1})$ in acetonitrile were obtained from the Stern–Volmer constants K_q and the emission lifetime in the absence of quencher, τ_0 .²⁰

Results and Discussion

Photooxidation of DBT and DMDBT Sensitized by NMQ^+ . Photooxidation of DBT and DMDBT sensitized by NMQ^+ was carried out in O_2 -saturated acetonitrile solutions and was monitored by HPLC (Figure 1 and Figure 2). Each product is well identified by the mass spectra (MS). No reaction took place without NMQ^+ or UV irradiation, as confirmed by control experiments. In the photooxidation of DBT, the products are dominantly composed of DBT sulfoxide and sulfone, as shown in Figure 1. This is different from the case of the sulfides with α -H, for which only sulfoxides were produced in the photooxidation.¹³ Moreover, sulfone continued to be formed after DBT was completely consumed, revealing that sulfone originates

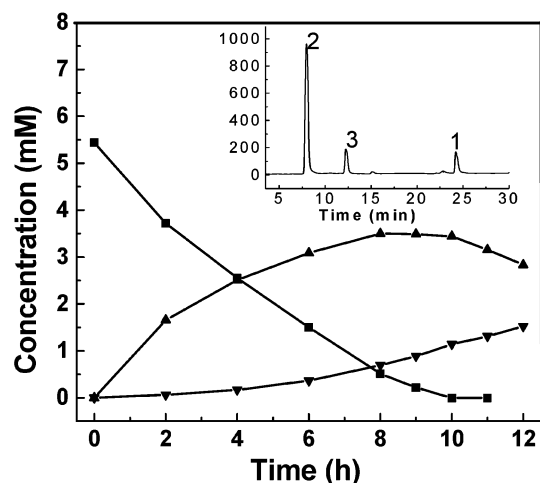


Figure 1. Changes in concentrations of DBT (■), DBT sulfoxide (▲), and DBT sulfone (▼) versus the irradiation time in the NMQ^+ (2.7×10^{-4} M)-sensitized photooxidation of DBT (5.4×10^{-3} M) in O_2 -saturated acetonitrile solution. Inset: The HPLC chromatogram of the photooxidation products of DBT after 6 h.

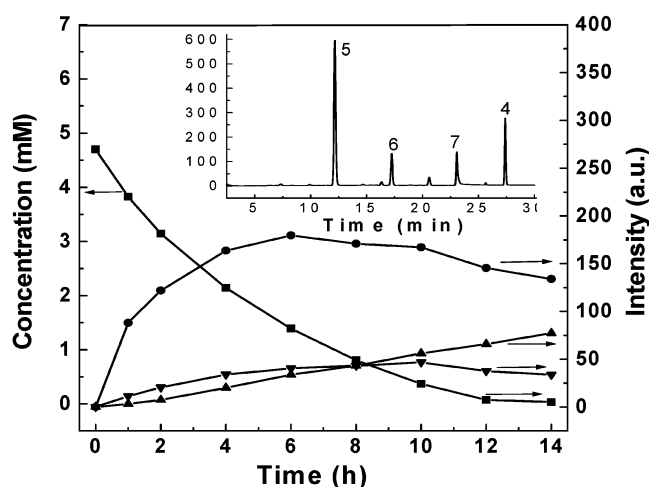
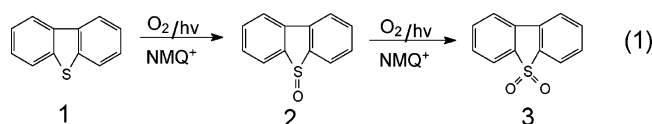


Figure 2. Changes in concentrations of DMDBT (■), DMDBT sulfoxide (●), DMDBT sulfone (▲), and compound 7 (▼) versus the irradiation time in the NMQ^+ (2.3×10^{-4} M)-sensitized photooxidation of DMDBT (4.6×10^{-3} M) in O_2 -saturated acetonitrile solution. Inset: The HPLC chromatogram of the photooxidation products of DMDBT after 4 h.

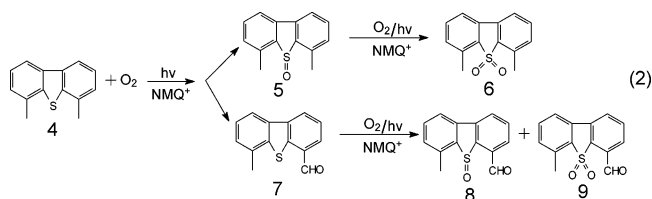
from some reaction intermediate, most likely the sulfoxide (eq 1). This was inferred by the experiment with sulfoxide as the



initial reactant (see below). Sulfone was obviously the final product, since no reaction was detected for the otherwise identical photoreaction system but with DBT sulfone as the initial reactant.

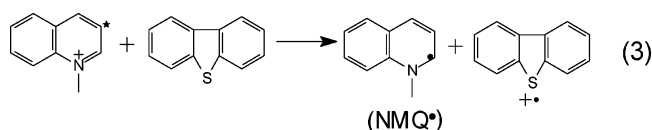
Similar to the case of DBT, DMDBT could also be efficiently oxidized, producing both corresponding sulfoxide and sulfone. Continuous formation of sulfone was also found after DMDBT was completely consumed. What was observed differently from the case of DBT is that one more product 7 was detected from the reaction of DMDBT. The new product was identified by both MS²¹ and IR spectrum²² (Figure 2). Interestingly, 7 could be slowly oxidized further to 8 and 9 with extended irradiation

time (as shown in eq 2). These products were separated by HPLC and then were analyzed by MS.



The Formation of Sulfoxides via Photoinduced ET Mechanism. The fluorescence lifetime of NMQ^+ decreased in the presence of DBT and DMDBT. The bimolecular rate constants k_q ($=K_q\tau_0^{-1}$), $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (DBT) and $2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (DMDBT), are obtained from the Stern–Volmer constants K_q and the intrinsic fluorescence lifetime τ_0 of NMQ^+ in acetonitrile. The fluorescence quenching observed herein should be due to an ET mechanism, since there is little possibility for energy transfer from the excited NMQ^+ to the quenchers (i.e., no overlap between the emission band of the excited NMQ^+ and the absorption band of the quenchers).

The ET process between the substrates and the excited states of NMQ^+ was also investigated by using laser flash photolysis (LFP) with excitation at 355 nm, as shown in Figure 3. Both transient absorption spectra and decay kinetics were obtained for the acetonitrile solutions of NMQ^+ containing DBT or DMDBT. The experiments were carried out under both Ar and O_2 saturated conditions. In Ar-saturated solutions of DBT and NMQ^+ , a transient absorption band centered at 550 nm was observed, and the absorption decays on a time scale of microseconds (Figure 3A). The transient absorption is attributable to the neutral radical NMQ^\bullet ,¹³ which is formed via electron transfer from DBT to the excited-state NMQ^{+*} (eq 3). Unfor-



unately, we were not able to detect the transient absorption of the cationic radical of DBT formed in the same ET process. This might be due to the weak absorptivity of the radical or the overlap of the absorption bands. It was also found that the absorption decay recorded at 550 nm was well fitted by second-order kinetics ($k/\epsilon = 6.9 \times 10^6 \text{ s}^{-1} \text{ cm}$) under Ar-saturated conditions.

In the presence of oxygen, the decay became so fast that no pronounced absorption band could be observed (Figure 3B). This indicates a rapid charge-transfer reaction between NMQ^\bullet and O_2 .

When DMDBT was used instead of DBT, the same transient absorption band of NMQ^\bullet centered at 550 nm was observed. The absorption decay was also well fitted by second-order kinetics in the absence of O_2 ($k/\epsilon = 1.11 \times 10^7 \text{ s}^{-1} \text{ cm}$). Again, in the presence of oxygen, it was hard to detect the absorption of NMQ^\bullet radical due to the fast charge transfer from NMQ^\bullet to O_2 (see Supporting Information, S1).

The ET reaction between NMQ^\bullet and O_2 can be further confirmed by the ESR measurements. Figure 4A shows the typical signals of $\text{O}_2^{\bullet-}$ trapped by DMPO (i.e. $\text{DMPO-O}_2^{\bullet-}$),^{23–25} which was obtained in the irradiated solution of DBT containing NMQ^+ as the sensitizer and oxygen as the radical scavenger. To the best of our knowledge, this is the first ESR measurement showing the formation of $\text{O}_2^{\bullet-}$ activated by NMQ^\bullet .

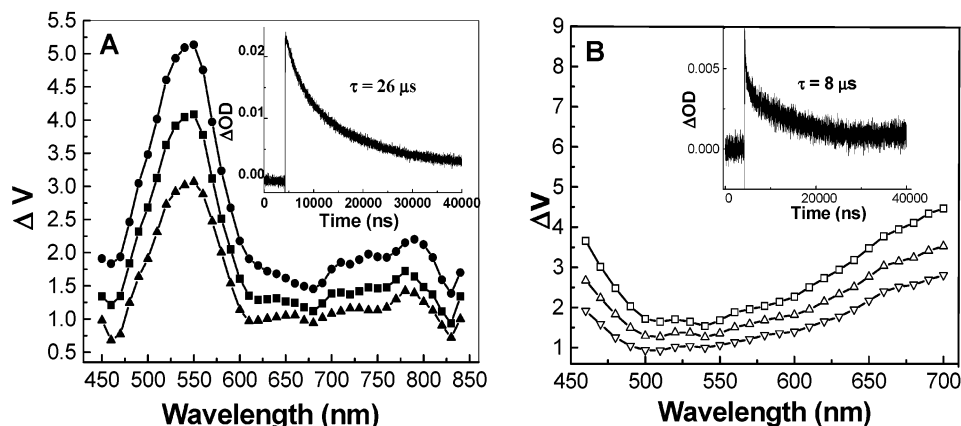


Figure 3. Transient absorption spectra of the NMQ^+/DBT system (1.1×10^{-3} and 5.4×10^{-3} M, respectively) in acetonitrile: (A) Ar-saturated, spectra were recorded at 8 (●), 12 (■), and 20 μs (▲) after the laser pulse; (B) O_2 -saturated, spectra were recorded at 2 (□), 4 (Δ), and 8 μs (▽) after the laser pulse ($\lambda = 355$ nm). Inset: Decay kinetics recorded at 550 nm.

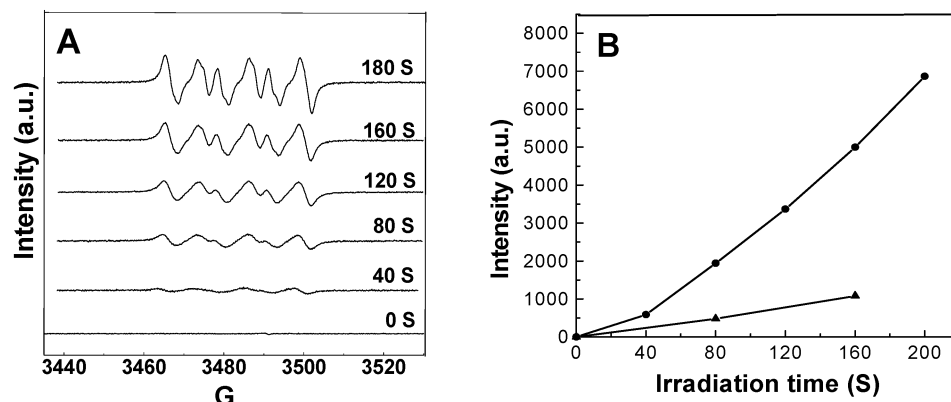
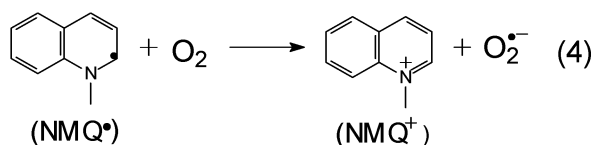
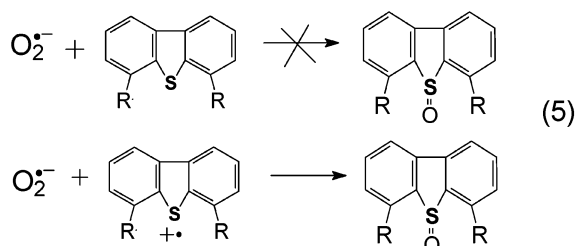


Figure 4. (A) ESR spectral variance with the irradiation time in the NMQ^+ (1.1×10^{-3} M)-sensitized photooxidation of DBT (5.4×10^{-3} M) with oxygen. (B) Plots of ESR signal intensity as a function of irradiation time: without BQ (●) and with BQ (3.7×10^{-3} M) (▲).

radicals, although such a reaction has been proposed previously in the literature.^{26,27} The observed ESR spectra indicate that molecular oxygen can efficiently trap one electron from NMQ^* to form $\text{O}_2^{\bullet-}$ and recover NMQ^+ (eq 4). The same ESR signal of $\text{DMPO}-\text{O}_2^{\bullet-}$ was also detected in the otherwise identical solution but with DMDBT.



To further confirm that the formation of sulfoxide is from the reaction between $\text{O}_2^{\bullet-}$ and the substrate radical cation, the reaction of the substrates with KO_2 (control experiments) was investigated in acetonitrile. No sulfoxides were thus formed, indicating that sulfoxides were likely formed via the reaction of $\text{O}_2^{\bullet-}$ with the substrate radical cations (eq 5).



Another strong piece of evidence for the ET mechanism in the NMQ^+ -sensitized photooxidation was obtained by carrying

TABLE 1: Photooxidation of DBT Sensitized by NMQ^+ in O_2 -Saturated Acetonitrile Solutions^a

entry	substrate (mM)	additive (mM)	irradiation time (h)	products (μmol)	
				sulfoxide	sulfone
1	DBT (5.4)		2	33.20	0.26
2	DBT (5.4)	BQ (3.7)	2	1.72	0.05
3	DBT (5.4) ^b	Eosin	10	0.77	0.15

^a Volume: 20 mL. In all cases, the sensitizer concentration was 5 mol % (to the substrate). ^b In O_2 -saturated acetonitrile solution of Eosin.

TABLE 2: Photooxidation of DMDBT Sensitized by NMQ^+ in O_2 -Saturated Acetonitrile Solutions^a

entry	substrate (mM)	additive (mM)	irradiation time (h)	products ^b		
				sulfoxide	sulfone	7 ^c
1	DMDBT (4.7)		2	121.94	7.41	20.58
2	DMDBT (4.7)	BQ (3.7)	2	4.32	1.21	17.82
3	DMDBT (4.7)	Eosin	10	5.62	0.75	0

^a Volume: 20 mL. ^b The intensity (au) in HPLC chromatogram. ^c Compound 7 produced in photooxidation of DMDBT (Figure 2).

out the photooxidation reaction in the presence of benzoquinone (BQ), an effective trap for NMQ^* and $\text{O}_2^{\bullet-}$.²⁸ As shown in Table 1, entry 2, and Table 2, entry 2, the formation of DBT sulfoxide and DMDBT sulfoxide was greatly suppressed by BQ. This is also in agreement with the variance of the ESR spectra of $\text{O}_2^{\bullet-}$ trapped by DMPO obtained under the same conditions (Figure 4B). Upon addition of more BQ (7×10^{-3} M), the photooxidation reaction was almost completely suppressed.

Since $^1\text{O}_2$ can be produced by $^1\text{NMQ}^*$,¹³ the role of $^1\text{O}_2$ in the formation of sulfoxides was also investigated. The photo-

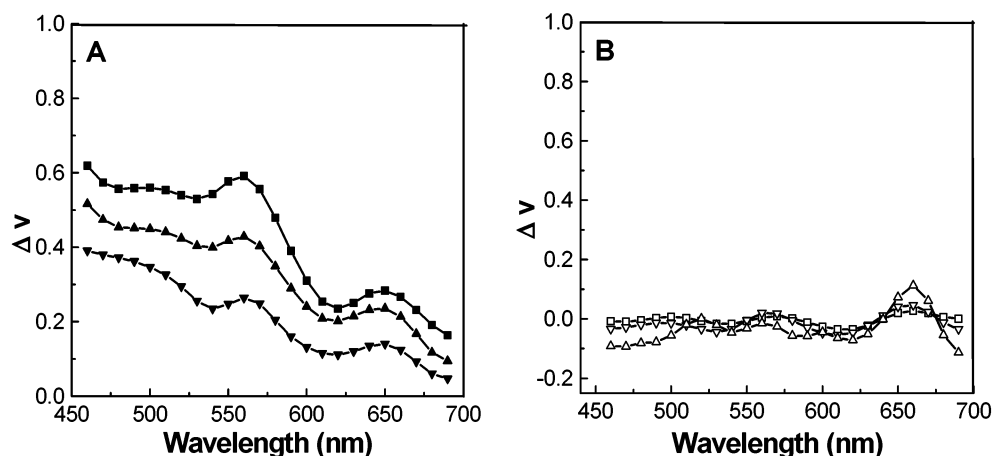


Figure 5. Transient absorption spectra of the NMQ^+ /DBT sulfoxide system (1.1×10^{-3} and 3.5×10^{-3} M, respectively) in acetonitrile: (A) under Ar-saturated condition, spectra were recorded at 6 (■), 7 (▲), and 9 μs (▼) after the laser pulse; (B) under O_2 -saturated condition, spectra were recorded at 2 (□), 5 (△), and 10 μs (▽) after the laser pulse ($\lambda = 355$ nm).

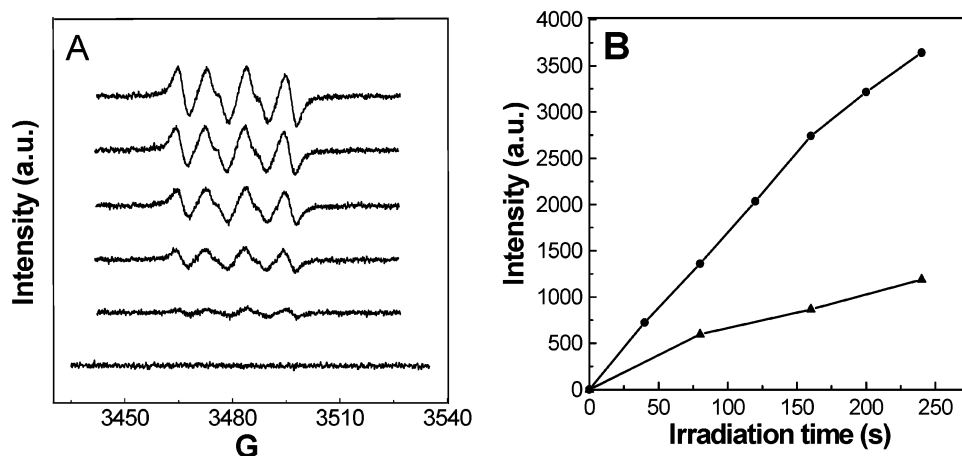


Figure 6. (A) ESR spectral variance with the irradiation time in the photooxidation of DBT sulfoxide (3.5×10^{-3} M) sensitized by NMQ^+ (1.1×10^{-3} M) with O_2 . (B) ESR signal intensity as a function of irradiation time: without BQ (●) and with BQ as a trap (3.7×10^{-3} M) (▲).

oxidation of DBT and DMBT sensitized by Eosin, an effective sensitizer for $^1\text{O}_2$, was conducted in acetonitrile solution by irradiation under O_2 -saturated conditions. However, neglectable contribution was observed to the formation of DBT or DMBT sulfoxide (Table 1, entry 3, and Table 2, entry 3).

Thus, it can be concluded that in the NMQ^+ -sensitized photooxidation of DBT and DMBT, the formation of sulfoxides is via a photoinduced ET mechanism, in which the sensitizer plays a critical role as electron relay.

The Formation of Sulfones via Photoinduced ET Mechanism. Figures 1 and 2 show that sulfones continued to be formed after the substrates were completely consumed. To probe the reaction mechanism, the transient absorption spectra were obtained upon laser flash irradiation of Ar-saturated and O_2 -saturated acetonitrile solution containing NMQ^+ and DBT sulfoxide as the initial reactants. As shown in Figure 5A, the absorption band centered at ca. 550 nm could still be observed, which indicates the formation of NMQ^* . This implies the possibility of an electron-transfer reaction from DBT sulfoxide to the excited state of NMQ^+ . In the presence of O_2 , no apparent transient absorption of NMQ^* appeared, mostly due to the efficient quenching of NMQ^* by O_2 (Figure 5B). As further inferred from the ESR experiments, the ET mechanism is also operating in the photooxidation of DBT sulfoxide sensitized by NMQ^+ in the presence of oxygen. Figure 6A illustrates the spin-trap ESR pattern in the NMQ^+ -sensitized photooxidation of DBT sulfoxide with oxygen. The typical signal of DMPO—

TABLE 3: Photooxidation of DBT Sulfoxide (DBTO) and DMBT Sulfoxide (DMBTO) Sensitized by NMQ^+ in O_2 -Saturated Acetonitrile^a

entry	substrate (mM)	additive (mM)	irradiation time (h)	products (μmol) sulfone
1	DBTO (3.1)		1	4.50
2	DBTO (3.0)	BQ (3.7)	1	0.93
3	DMBTO ^b		2	11.38 ^c
4	DMBTO ^b	BQ (3.7)	2	2.98 ^c

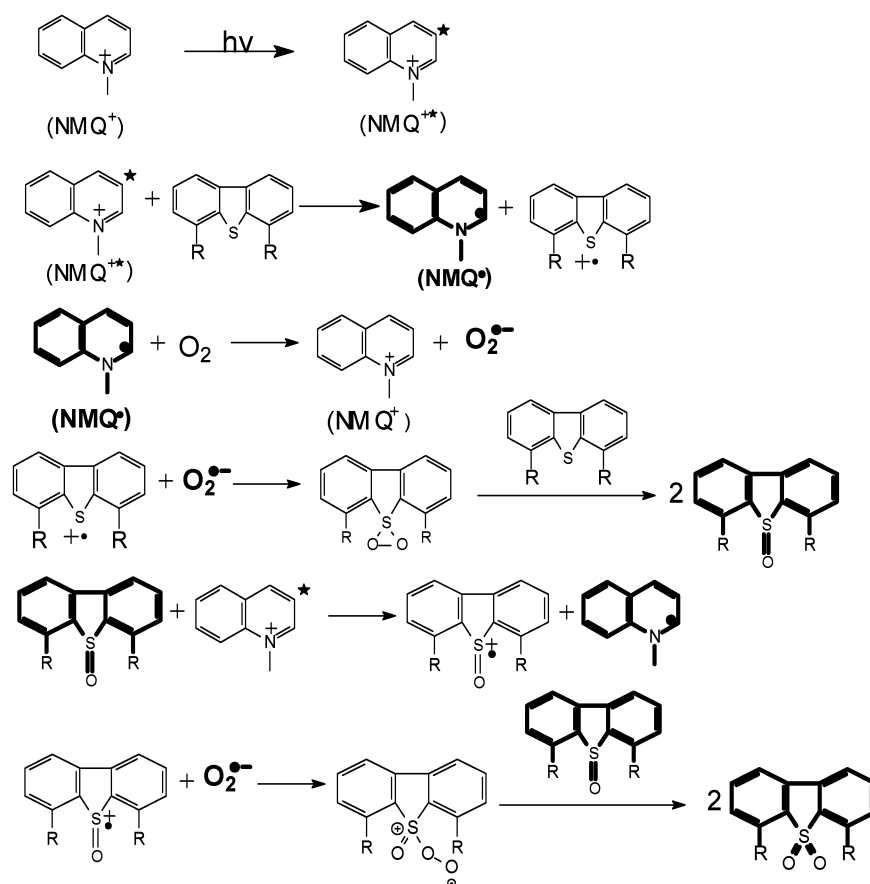
^a Volume: 20 mL. ^b Approximately equivalent area of DMBTO after DMBT was completely oxidized. ^c The intensity (au) in HPLC chromatogram.

$\text{O}_2^{\bullet-}$ indicates the occurrence of ET reaction from NMQ^* to O_2 . The formation of sulfones via the reaction of $\text{O}_2^{\bullet-}$ with sulfoxide cationic radical is inferred from the trapping experiment by BQ. In the presence of BQ, the formation of sulfones dramatically decreased (Table 3), which is in agreement with the variance of the ESR spectra of $\text{O}_2^{\bullet-}$ trapped by DMPO (Figure 6B).

The ESR spectrum observed in the case of DMBT sulfoxide is similar to those obtained for DBT sulfoxide. The only difference is the change of the intensity of the ESR signals (see Supporting Information, S3). Thus, it is certain that sulfones are formed via the photoinduced ET mechanism mediated by NMQ^+ and O_2 .

In addition, the photooxidation of DMBT is a little more complicated than that of DBT. One more product was formed

SCHEME 3



(compound **7**, Figure 2) in the former case. Addition of BQ showed no significant effect on the formation of **7** (Table 2, entry 2), which suggests O₂^{•-} contributes little to the formation of the compound. Moreover, no **7** was detected in the absence of either NMQ⁺ or irradiation. We propose that the formation of **7** in the photooxidation of DMDBT is initiated by the similar ET mechanism in the literature.^{29,30}

It can now be concluded that an ET mechanism is operating in the NMQ⁺-sensitized photooxidation of DBT and DMDBT with O₂. In addition, both sulfoxides and sulfones were formed, just like the case of ¹O₂ photooxidation of sulfides. Does the similar product distribution suggest that similar reaction intermediates are formed? In ¹O₂ photooxidation of sulfides, the initially formed key intermediate has been suggested to be the persulfide (Scheme 1), which can then be converted to a second reaction intermediate, probably a *S*-hydroperoxysulfonium ylide in aprotic solvents. The ylide species can not only efficiently oxidize sulfides to sulfoxides but also self-rearrange to sulfones.^{9–11} In ¹O₂ photooxidation of sulfides, another important piece of evidence for the formation of persulfides

is the dramatic acceleration of the photooxidation by protic solvents.^{2,5} However, in the NMQ⁺-sensitized photooxidation of DBT and DMDBT, there is no possibility for the *S*-hydroperoxysulfonium ylide to be formed from the corresponding persulfide **10** due to the lack of α-H in both DBT and DMDBT. Therefore, there should be another reaction pathway in the photooxidation of DBT and DMDBT compared to the case of ¹O₂ photooxidation. Moreover, no acceleration of the formation of sulfoxides was observed but the absolutely contrary case occurred when some water was added to the NMQ⁺-sensitized photooxidation of DBT and DMDBT, as shown in Tables 4 and 5. Such a deceleration of the formation of

TABLE 4: Effect of the Addition of Water on the Photooxidation of DBT Sensitized by NMQ⁺ in O₂-Saturated Acetonitrile^a

entry	substrate (mM)	irradiation time (h)	products (μmol)	
			sulfoxide	sulfone
1	DBT (5.4)	2	33.23	0.26
2	DBT (5.4)	4	50.21	0.69
3	DBT (5.4) ^b	2	21.08	0.13
4	DBT (5.4) ^b	4	30.14	0.35

^a Volume: 20 mL. In all cases, the sensitizer concentration was 5 mol % (to the substrate). ^b Addition of water (5 v %).

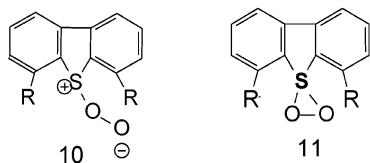
TABLE 5: Effect of the Addition of Water on the Photooxidation of DMDBT Sensitized by NMQ⁺ in O₂-Saturated Acetonitrile^a

entry	substrate (mM)	irradiation time (h)	products (area) ^c	
			sulfoxide	sulfone
1	DMDBT (4.7)	2	121.94	7.41
2	DMDBT (4.7)	4	163.75	20.05
3	DMDBT (4.7) ^b	2	51.08	0
4	DMDBT (4.7) ^b	4	64.87	1.53

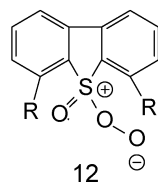
^a Volume: 20 mL. In all cases, the sensitizer concentration was 5 mol % (to the substrate). ^b Addition of water (10 v %). ^c The intensity (au) in HPLC chromatogram.

sulfoxides may be ascribed to the reaction between water and O₂^{•-},³¹ which leads to a smaller amount of **11** being formed. This further rules out the possibility of **10** as the intermediate. In our case, the only possible intermediate directly formed from DBT or DMDBT radical cation and O₂^{•-} is the electrophilic cyclic thiadioxirane **11**.³¹ Although cyclic thiadioxirane as the second intermediate has also been discarded on the basis of

calculations in $^1\text{O}_2$ photooxidation,¹⁴ the direct formation of cyclic thiadioxirane by a radical cation and $\text{O}_2^{\bullet-}$ has been implied by theoretical calculations.¹³ Here, the electrophilic property of **11** can reasonably explain the formation of sulfoxides in the photooxidation of DBT and DMDBT.



The results discussed above allowed us to conclude that it is impossible for sulfones to be formed intramolecularly via S-hydroperoxysulfonium ylide like the case of $^1\text{O}_2$ photooxygenation of sulfides. Figures 1 and 2 show that almost no sulfones were formed in the first 2 h and that sulfones continued to be formed after DBT and DMDBT were consumed. This means that sulfones were formed from the photooxidation of sulfoxides. Laser flash photolysis and ESR experiments demonstrate that the ET mechanism operates in the photooxidation of sulfoxides, although it failed to detect a plausible intermediate formed from sulfoxide cationic radical cation and $\text{O}_2^{\bullet-}$. Here, the intermediate is primarily proposed as **12** in the light of its nucleophilic character.³² A nucleophilic O transfer by **12** would lead to the formation of sulfones in the photooxidation of sulfoxides.



Overall Mechanism. Based on all the above results, the overall mechanism for the formation of sulfoxides and sulfones is outlined in Scheme 3. The structures with bold label have been identified in our experiments.

Conclusion

The use of NMQ^+ as a photosensitizer has enabled us to accomplish nearly 100% photooxygenation of DBT and DMDBT. The products are dominantly composed of sulfoxides and sulfones. The sulfones originate from the further photooxidation of sulfoxides. For the photooxidation of DMDBT, one more product **7** is generated compared to the case of DBT. The observed transient absorption spectra of NMQ^{\bullet} and the ESR spectra of $\text{O}_2^{\bullet-}$ trapped by DMPO as well as the trapping experiments with BQ lead to a conclusion that the formation of both sulfoxides and sulfones is attributable to a photoinduced ET mechanism. Due to the lack of $\alpha\text{-H}$ in DBT and DMDBT, there is no possibility for the formation of S-hydroperoxysulfonium ylides, which has been proposed as a crucial intermediate in $^1\text{O}_2$ photooxidation. The electrophilic cyclic thiadioxirane and the nucleophilic intermediate **12** are proposed to be responsible for the formation of sulfoxides and sulfones, respectively.

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Supporting Information Available: Transient absorption spectra of the $\text{NMQ}^+/\text{DMDBT}$ system (Figure S1), and ESR spectral variance with the irradiation time in the NMQ^+ -sensitized photooxidation of DMDBT (Figure S2) and DMDBT sulfoxide (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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