Visible Photooxidation of Dibenzothiophenes Sensitized by 2-(4-Methoxyphenyl)-4, 6-diphenylpyrylium: An Electron Transfer Mechanism without Involvement of Superoxide

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Received: September 16, 2005; In Final Form: December 11, 2005

We report here on a new electron-transfer mechanism for visible-light photooxidation of sulfides in which no superoxide ion is involved. Visible-light irradiation of 2-(4-methoxyphenyl)-4, 6-diphenylpyrylium tetrafluoroborate ($MOPDPP^+BF_4^-$) in an O_2-saturated acetonitrile solution containing dibenzothiophene (DBT) results in nearly 100% conversion to oxygenated products, DBT sulfoxide and sulfone. The photooxidation of DBT is initiated by a photoinduced electron-transfer process, where the excited $MOPDPP^+$ traps an electron from the ground-state DBT to form $MOPDPP^•$ and DBT radical cation. Such a mechanism is consistent with the studies of laser flash photolysis, electron spin resonance, and fluorescence quenching of the irradiated system. The photogenerated DBT radical cation undergoes a coupling reaction with O_2 to produce the intermediate responsible for the formation of the oxygenated products. The presence of O_2 has no effect on the decay kinetics of the transient absorption of $MOPDPP^•$, indicating that no redox reaction occurs between $MOPDPP^•$ and O_2, and thus no superoxide ion ($O_2^{•-}$) is formed. Moreover, the ESR signal of $MOPDPP^•$ was significantly enhanced in the presence of O_2, consistent with the assumption that the photogenerated DBT radical cation couples with O_2 to form the oxygen-adduct, which is subject to further reactions (Scheme 3) leading to the final oxygenated products. Similar results have been obtained when using 10-methylacridine hexafluorophosphate ($AcrH^+PF_6^-$, which has similar reduction potential in the ground state as $MOPDPP^+$) as the sensitizer. This finding provides a possibility for the photooxidation of sulfides with dioxygen utilizing visible light (solar energy) and is also of significance in clarification of the reaction mechanism.

Introduction

Sulfide oxidation has attracted intense interest in view of biological implications,[1] practical application in synthesis,[2] and desulfurization of light oil.[3] Most of the oxidation reactions are mediated by direct oxygen transfer. The main oxidants used are limited to hydroperoxide,[4−7] alkylperoxide,[4,8] peroxynitrous acid,[9,10] and transition-metal-based oxidants.[11,12] Only in a few examples of transition-metal-based catalysts has molecular oxygen been used as an oxidant for sulfide oxidation.[13] Compared to these typical oxidants, molecular oxygen is an ideal and unique oxidant from the point of view of operation cost and potential pollution to the environment.[14] However, oxidation of organic substrates with O_2 is usually kinetically inhibited due to the triplet ground state of O_2.[15] One way to initiate the oxidation is to activate molecular oxygen to the active species such as singlet oxygen ($^1O_2$) and superoxide ion ($O_2^{•-}$), while the other option is to transform the substrate compound to a species which can react with ground-state O_2.

Photochemistry has proven to be an effective method both to activate O_2 to $^1O_2$ and $O_2^{•-}$ via energy transfer and electron transfer (ET), respectively, and to transform the substrates to reactive radicals through ET reactions between the substrate and the excited photosensitizer. While sulfide oxidation through $^1O_2$ has been extensively studied and understood,[16−18] the oxidation through ET has not been extensively investigated, and the mechanism remains in debate.[19,20] Recently, Baciocchi et al.[21] have reported that the thiadioxirane intermediate is responsible for mediating the ET initiated and the $O_2^{•-}$ involved photooxidation of dibutyl sulfide and thioanisole. This is different from the mechanism of $^1O_2$ oxidation, where the persulfoxide is deemed to be the key intermediate involved.[22] However, the oxidation via $^1O_2$ may compete with the ET mediated oxidation, since many organic sensitizers used for photoinduced ET are also efficient for photogenerating $^1O_2$. For the sulfides with α-H, which are highly reactive to $^1O_2$, the involvement of $^1O_2$ could make it difficult to determine the intermediates assigned to the ET-mediated photooxidation. Recently, we have chosen dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) as the model molecules to investigate the photooxidation under UV irradiation.[23] The sensitizer used was *N*-methylquinolinium (NMQ^+) with absorption maximum at 317 nm. Both of the two model compounds have no α-H and thus are inert to $^1O_2$. This makes a relatively simple reaction system to investigate the ET mediated photooxiation. The observation indicated that $O_2^{•-}$ was generated by the reaction between molecular oxygen and the photogenerated radical of the sensitizer, $NMQ^•$. The reaction of $O_2^{•-}$ with the sulfide radical cation produced the thiadioxirane intermediate, which was assumed to be the critical intermediate for further oxidation (Scheme 1).

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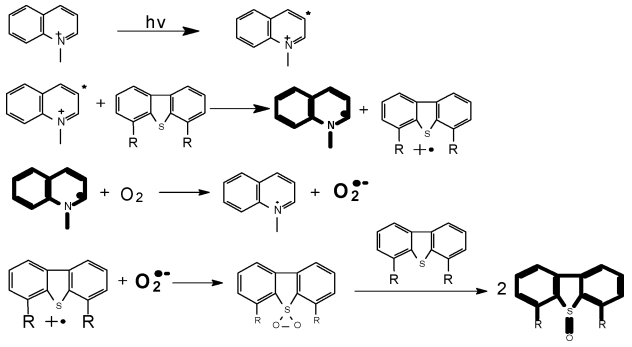
10.1021/jp055261f CCC: $33.50
Published on Web 01/19/2006

SCHEME 1

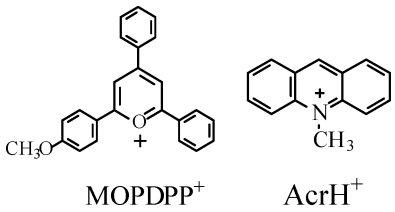


The major goal of the current research in sulfide photooxidation would be either to extend the practical application by finding some effective sensitizers working in the visible region, or to clarify the reaction mechanism (via $^3O_2$, $^1O_2$, or $O_2^{\bullet-}$) by setting up a simple and neat reaction system. Most of the sensitizers used up to date, such as dicyanobenzenes and iminium ions, work in the UV region. This limits the practical utilization of solar energy. Additionally, the UV irradiation may lead to direct excitation of the substrate compounds and thus cause undesired reactions.[24] It is, therefore, imperative to find a sensitizer that can effectively operate under visible irradiation. On the other hand, to simplify the reaction mechanism of photooxidation, we may select a sensitizer with such appropriate energy levels that the ET from the photogenerated radical of the sensitizer to molecular oxygen is not favored and thus the formation of $O_2^{\bullet-}$ is negligible. This will lead to a simple oxidation pathway only involving molecular oxygen (triplet or singlet state). Another way to simplify the reaction mechanism is to select appropriate substrate compounds for oxidation. Through appropriate selection of both sensitizer and substrate compounds, it would be possible to observe an ET mediated photooxidation with the involvement of only triplet (ground state) oxygen. *However, there has been no such ET photooxidation reported up to date.*

In this work, the photooxidation of DBT and DMDBT with O_2 has been investigated using a visible sensitizer, 2-(4-methoxyphenyl)-4,6-diphenylpyrylium ($MOPDPP^+$), which has an absorption maximum at ca. 450 nm.[25] Due to the high reduction potential in its excited state ($E^*_{red} = 2.0$ V vs SCE)[26] compared to the oxidation potential of DBT ($E_{ox} = 1.8$ V vs SCE) and DMDBT ($E_{ox} = 1.7$ V vs SCE), $MOPDPP^+$ could be an efficient sensitizer to initiate the photooxidation of the two substrate compounds through photoinduced ET from the substrates to the excited $MOPDPP^+$ according to the Rehm−Weller equation.[27] More interestingly, the ET from the thus formed sensitizer radical to molecular oxygen is an endergonic process and, therefore, there will be little $O_2^{\bullet-}$ formed. Also, the two substrate compounds selected are inert to singlet oxygen as proved in our previous work,[23] and the involvement of singlet oxygen in the photooxidation is negligible. The efficient photooxidation observed must be due to a new mechanism that involves only triplet (ground state) oxygen. Such an observation is highly complementary to the understanding of ET mediated photooxidation of sulfides. To further clarify the reaction mechanism and process of $MOPDPP^+$-sensitized photooxidation, a UV sensitizer, 10-methylacridinium ($AcrH^+$), was also used for the photooxidation of the same compounds. $AcrH^+$ is known as an effective ET photosensitizer[28,29] and has the reduction potential in the ground state similar to that of $MOPDPP^+$.

Experimental Section

Materials. Dibenzothiophene (DBT) and 4, 6-dimethylbenzothiophene (DMDBT) were purchased from Aldrich and 2-(4-Methoxyphenyl)-4, 6-diphenylpyrylium tetrafluoroborate ($MOPDPP^+BF_4^-$) was purchased from Acrôs. They were all used as received. 10-Methylacridine iodide was synthesized by reaction of acridine with methyl iodide in acetone. The iodide salt thus obtained was converted to the hexafluorophosphate salt ($AcrH^+PF_6^-$) in water by the addition of ammonium hexafluorophosphate. Acetone and acetonitrile were of analytical reagent-grade and used as purchased.



$MOPDPP^+$ $AcrH^+$

Photooxidation Procedure. The photooxidation of DBT (5.4×10^{-3} M) and DMDBT (4.6×10^{-3} M) sensitized by $MOPDPP^+$ (8% mol) was carried out in an oxygen-saturated (0.08 Mpa) acetonitrile solution contained in a cylindrical borosilicate glass flask. A 500W halogen lamp was used as light source, and was positioned inside a cylindrical borosilicate glass jacket surrounded by circulating water to cool the lamp and to minimize infrared radiation. A cutoff filter was placed outside the borosilicate glass jacket to completely eliminate any irradiation below 420 nm, ensuring illumination by visible light only. The distance between the light source and the flask was about 10 cm. Oxidation products were detected by HPLC (Dionex P580 pump and UVD340S diode array detector) using an Intersil ODS-3C-18 inversed-phase column. The eluent gradient was regulated by water and acetonitrile. For the photooxidation products of DBT, the acetonitrile gradient was adjusted from 40 to 80% in the first 20 min and from 80 to 100% in the next 10 min. For the case of DMDBT, the acetonitrile gradient was adjusted 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 a Finnigan Trace DSQ instrument. The UV−vis absorption spectra of $MOPDPP^+$ before and after the reaction were recorded using a Hitachi U-3010 spectrophotometer. The same procedure was applied to the photooxidation reaction using $AcrH^+$ as the photosensitizer except the light source. A 100W Hg lamp (TOSHIBA Lighting and Technology Corporation, Japan) was used as the UV light source.

ESR Measurements. The electron spin resonance (ESR) spectra were obtained on a Bruker model E-500 electron paramagnetic resonance spectrometer equipped with a Quanta-Ray Nd:YAG laser system. An O_2- or Ar-saturated acetonitrile solution of $MOPDPP^+$ (1.4×10^{-3} M) and DBT (1.1×10^{-2} M) was irradiated at 77 K with the laser beam at 532 nm. The settings were as follows: center field, 3440.00 G; microwave frequency, 9.79 GHz; power, 20.1 mW. The *g* values were calibrated by using diphenyl picryl hydrazyl as the standard. Similarly, the ESR spectra of the sample of $AcrH^+$ (2.6×10^{-3} M) and DBT (1.1×10^{-2} M) were recorded with laser irradiation at 355 nm.

Laser Flash Photolysis. The measurement of transient absorption spectra in the photooxidation of DBT with $MOPDPP^+$ or $AcrH^+$ in acetonitrile was performed using a nanosecond laser flash photolysis system. The acetonitrile

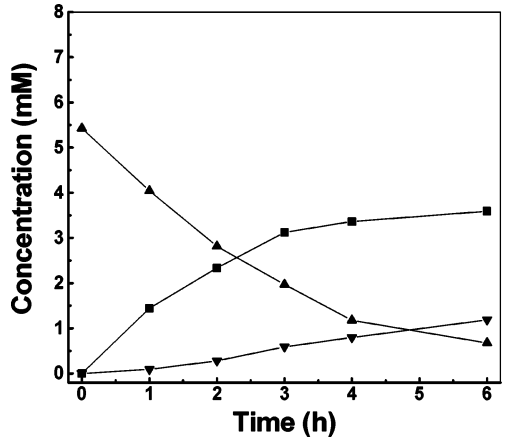


Figure 1. Changes in concentration of DBT (▲), DBT sulfoxide (■), and DBT sulfone (▼) versus the irradiation time in an O_2-saturated acetonitrile solution containing MOPDPP$^+$ (4.3×10^{-4} M) and DBT (5.4×10^{-3} M).

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, second harmonic) at 355 nm. The transient spectra were obtained by point-to-point recording (5 nm apart) of the absorbance change (V) at certain time intervals after the laser pulse. The spectra were recorded over the range of 400−800 nm. All measurements were performed at about 25 °C.

Fluorescence Quenching. Quenching experiments of the fluorescence of MOPDPP$^+$ or AcrH$^+$ by DBT were performed using a Hitachi F-4500 fluorometer. The excitation wavelength was 450 and 417 nm for MOPDPP$^+$ and AcrH$^+$, respectively. The solutions were deoxygenated by Ar purging for 15 min prior to the measurements. A linear Stern−Volmer relationship[30]

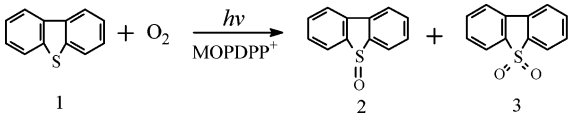
$$I_0/I = 1 + K_q[\mathrm{Q}]$$

was obtained for the investigated concentration range of the quenchers (Q). 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 of the photosensitizers in the absence of quencher, τ_0. The fluorescence lifetime of MOPDPP$^+$ in the absence of DBT was determined as 4.8 ns by single photon counting on a Horiba NAES-1100 time-resolved spectrofluorophotometer. The excitation wavelength was 450 nm and the emission wavelength was 550 nm.

Electrochemical Measurements. Electrochemical measurements were carried out on a Potentiostat/Galvanostat Model 283 electrochemical analyzer in deaerated acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$ as supporting electrolyte at 25 °C. Two platinum slices were used as the working and counter electrodes. The potentials were measured with respect to the SCE reference electrode.

Results and Discussion

Photooxidation of DBT Sensitized by MOPDPP$^+$ and AcrH$^+$. Visible light irradiation ($\lambda \geq 420$ nm) of an O_2-saturated acetonitrile solution containing MOPDPP$^+$ (4.3×10^{-4} M) and DBT (5.4×10^{-3} M) produced two oxygenation products, DBT sulfoxide and DBT sulfone (eq 1). Figure 1 shows the reaction time profile of the photooxygenation of DBT, which was monitored by HPLC (Supporting Information, Figure S1). Each product was well identified by the mass spectra. As confirmed by control experiments, no reaction took place without MOPDPP$^+$ or visible light irradiation. The major component of the initial oxidation products is DBT sulfoxide, which is subject to further oxidation to DBT sulfone. This is consistent with the observation that DBT sulfone continued to form even after DBT was nearly consumed. These results are similar to what we observed previously when using NMQ$^+$, a UV photosensitizer, for the same photooxidations.[23] MOPDPP$^+$ seems quite stable upon prolonged visible irradiation in the presence of the substrate compound DBT. After 5 h of irradiation at >420 nm, the absorption of MOPDPP$^+$ changed only slightly. The photooxidation of DBT was also carried out using a UV photosentizer, AcrH$^+$, which has reduction potentials in the ground state similar to that of MOPDPP$^+$.[31,32] Upon irradiation at >310 nm, the same oxygenation products, DBT sulfoxide and DBT sulfone, were detected (Supporting Information, Figure S2).



(1)

Photoinduced Electron Transfer. The fluorescence of MOPDPP$^+$ ($\lambda_{max} = 550$ nm) was effectively quenched in the presence of DBT (Supporting Information, Figure S3). The quenching showed a linear Stern−Volmer plot, implying a pure quenching mechanism through either dynamic or static process. Considering the molecular characteristics of the fluorophore (cationic) and quencher (neutral), one could assume a dynamic process for the quenching. Taking the intrinsic fluorescence lifetime τ_0 (4.8 ns) of MOPDPP$^+$ in acetonitrile, a bimolecular rate constant k_q ($= K_q\tau_0^{-1}$), 2.4×10^{10} $M^{-1}s^{-1}$, was obtained from the Stern−Volmer constant K_q. The rate constant obtained indeed falls into the typical range for a diffusion controlled process. The quenching is mainly due to intermolecular electron transfer from DBT to the excited state of MOPDPP$^+$ (eq 2). The high driving force for the electron transfer is inferred from the reduction potential of MOPDPP^{+*} ($E^*_{red} = 2.0$ V vs SCE) and the oxidation potential of DBT ($E_{ox} = 1.8$ V vs SCE) (Supporting Information, Figure S4). Furthermore, an energy transfer from the excited MOPDPP$^+$ to DBT is ruled out because there is no overlap between the emission band of MOPDPP$^+$ and the absorption band of DBT. Efficient fluorescence quenching was also found for the UV sensitizer, AcrH^{+*}, for which a linear Stern−Volmer plot was also observed (Supporting Information, Figure S5). A bimolecular rate constant of 2.0×10^{10} $M^{-1}s^{-1}$ was obtained taking 31 ns as the lifetime of AcrH^{+*}.[33]

$$\mathrm{DBT} + \mathrm{MOPDPP}^{+}{}^{*}\ (\mathrm{AcrH}^{+}{}^{*}) \rightarrow \mathrm{DBT}^{\bullet+} + \mathrm{MOPDPP}^{\bullet}\ (\mathrm{AcrH}^{\bullet}) \quad (2)$$

To explore the electron-transfer mechanism mediated in the photooxidation of DBT with MOPDPP$^+$ and AcrH$^+$, the photogenerated transient species were detected by laser flash photolysis (LFP). Excitation of MOPDPP$^+$ with a nanosecond laser pulse (7 ns, 355 nm) in deaerated and aerated acetonitrile solutions containing DBT produced the transient absorption spectra as shown in Figure 2. Under deaerated conditions, the absorption band centered at 550 nm is observed, which is assigned to 2-(4-methoxyphenyl)-4, 6-diphenylpyrylium radical (MOPDPP$^\bullet$) since the excited state of MOPDPP$^+$ have the different transient absorption (Supporting Information, Figure S6) and DBT radical cation has no apparent absorption at 550 nm in the AcrH$^+$-DBT system. When O_2 was introduced to the MOPDPP$^+$-DBT system in acetonitrile, the absorption spectra

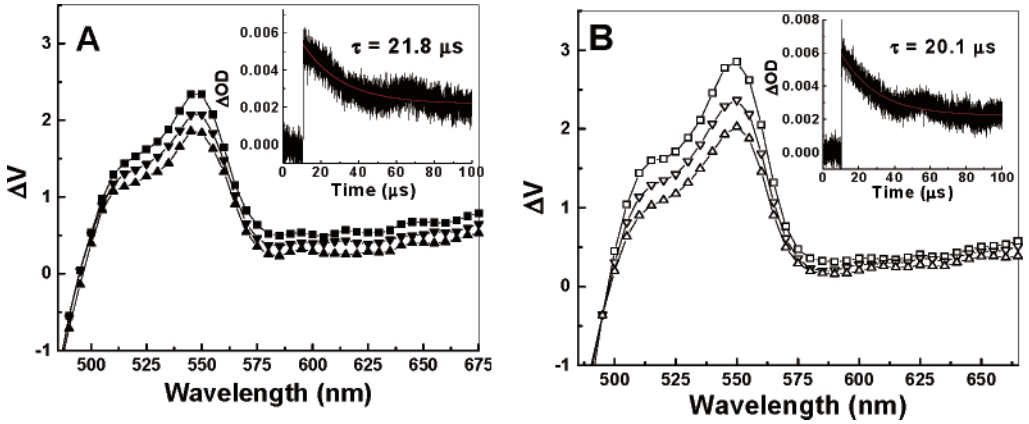


Figure 2. Transient absorption spectra of the acetonitrile solutions of MOPDPP$^+$ (3.0×10^{-5} M) containing DBT (5.4×10^{-3} M) excited with a pulsed laser at 355 nm: (A) Ar-saturated, spectra were recorded at 10 μs (■), 13 μs (▼), and 16 μs (▲) after the laser pulse; (B) O_2-saturated, spectra were recorded at 10 μs (□), 13 μs (▽), and 16 μs (△) after the laser pulse. Inset: single-exponential fitting of the absorption decay recorded at 550 nm.

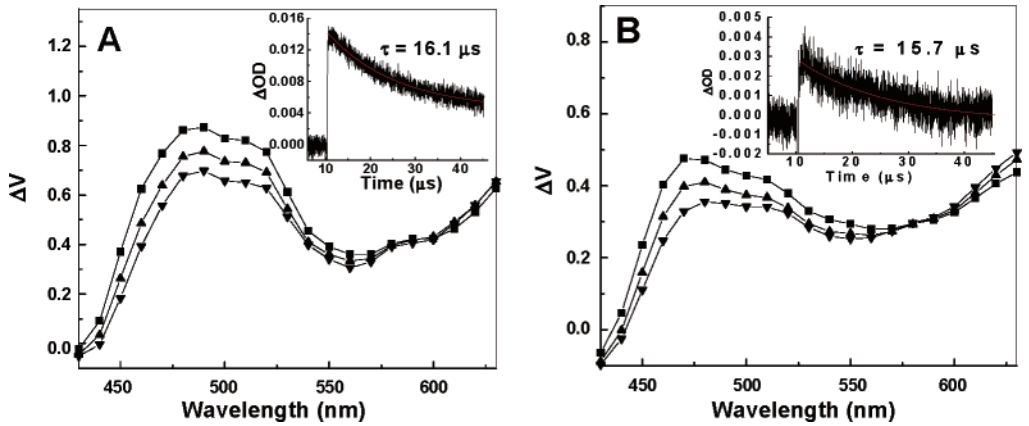


Figure 3. Transient absorption spectra of the acetonitrile solutions of AcrH$^+$ (1.2×10^{-4} M) containing DBT (1.1×10^{-2} M) excited with pulsed laser at 355 nm: (A) Ar-saturated, spectra were recorded at 10 μs (■), 15 μs (▲), and 20 μs (▼) after the laser pulse; (B) O_2-saturated spectra were recorded at 10 μs (■), 15 μs (▲), and 20 μs (▼) after the laser pulse. Inset: single-exponential fitting of the absorption decay recorded at 510 nm.

were similar to that observed under deaerated conditions (Figure 2B). It is important to note that the decay lifetime recorded at 550 nm did not reduce distinctively in the presence of O_2. This indicates clearly that O_2 has a negligible effect on the MOPDPP$^\bullet$ under the time-scale of the laser experiments.

The similar LFP investigation was also performed with the solutions of AcrH$^+$ containing DBT. Excitation at 355 nm resulted in the formation of 10-methylacridinyl radical (AcrH$^\bullet$), which has a broad absorption band between 450 and 545 nm,[34,35] as shown in Figure 3. Similarly, no appreciable changes of the decay lifetimes recorded at 510 nm were found in the presence and the absence of O_2, indicative of neglectable direct reaction between AcrH$^\bullet$ and O_2 under the time-scale of the laser experiments. Here, we cannot detect the transient absorption of the radical cation of DBT in both cases of AcrH$^+$ and MOPDPP$^+$ mediated photooxidation reactions, probably due to the weak absorptivity of the species or the overlap of the absorption bands. However, the direct observation of the transient absorption of AcrH$^\bullet$ and MOPDPP$^\bullet$ confirms the occurrence of ET from DBT to the singlet state of AcrH$^+$ and MOPDPP$^+$ to yield AcrH$^\bullet$ and MOPDPP$^\bullet$ as well as DBT radical cation.

To obtain further insight into the mechanism of photoinduced ET in the MOPDPP$^+$-sensitized photooxygenation of DBT, ESR spectra were measured for a irradiated, frozen acetonitrile solution (77 K) containing DBT and the photosensitizers. The measurements were carried out both in the absence and presence

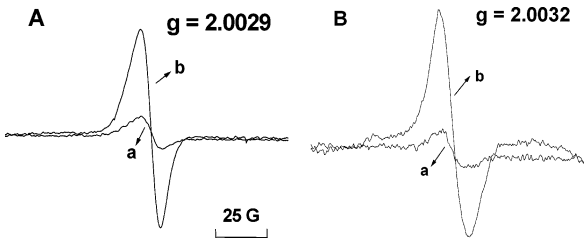


Figure 4. (A) ESR spectra observed under visible irradiation (λ = 532 nm) of an Ar-saturated (a) and O_2-saturated (b) acetonitrile solution of MOPDPP$^+$ (1.4×10^{-3} M) containing DBT (1.1×10^{-2} M) at 77 K; (B) ESR spectra observed under UV irradiation (λ = 355 nm) of an Ar-saturated (a) and O_2-saturated (b) acetonitrile solution of AcrH$^+$ (2.6×10^{-3} M) containing DBT (1.1×10^{-2} M) at 77 K.

of O_2. An ESR spectrum with g value of 2.0029 was obtained for the deaerated solution containing MOPDPP$^+$ and DBT, which was under laser irradiation at 532 nm (Figure 4A).

The detected signal could be due to either MOPDPP$^\bullet$ or DBT$^{+\bullet}$, which are both produced by the photoinduced ET (eq 2). Since the same signal was observed when DMDBT was used instead of DBT under the identical conditions, the signal can reasonably be assigned to MOPDPP$^\bullet$. The ESR spectrum of AcrH with g value of 2.0032 was also observed by laser excitation at 355 nm of a deaerated actonitrile solution containing DBT and AcrH$^+$ (Figure 4B) at 77 K. The ESR detection of MOPDPP$^\bullet$ and AcrH$^\bullet$ evidences the photoinduced ET process

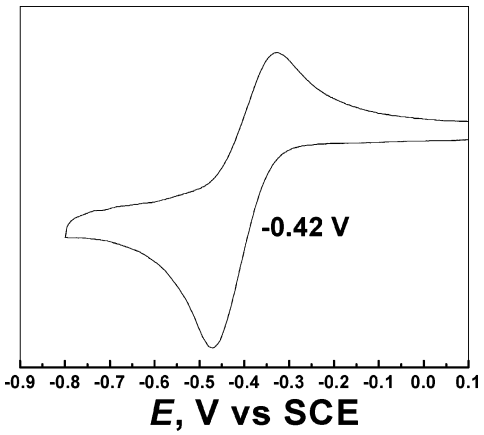


Figure 5. Cyclic voltammogram of $MOPDPP^+$ (1 mM) in a deaerated acetonitrile solution containing 0.1 M $Bu_4N^+PF_6^-$.

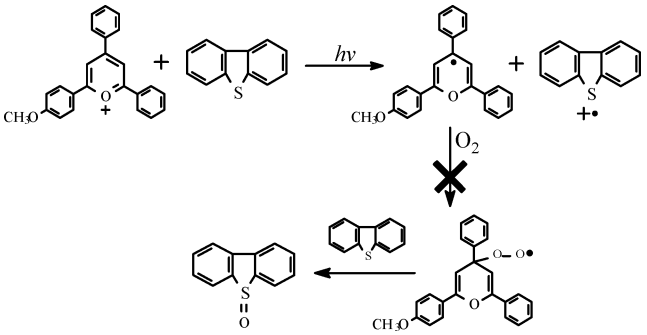
from DBT to the excited state of $MOPDPP^+$ or $AcrH^+$, as shown in eq 2. Moreover, in the presence of O_2 the ESR signal was dramatically increased, implying that O_2 does not react with the radicals of sensitizers. On the other hand, O_2 reacts effectively with DBT radical cation, thus preventing its recombination (back ET) with the radical of sensitizers. As a result, the signal of the sensitizer radical gets enhanced.

Photooxidation Mechanism. We have previously showed that the presence of singlet-oxygen ($^1O_2$) has negligible effect on the oxygenation of DBT and DMDBT,[23] so the mechanism of $^1O_2$ photooxidation can be ruled out in this study. Baciocchi et al. have recently found that the thiadioxirane intermediate formed from the reaction of a sulfide radical cation with $O_2^{\bullet-}$ is responsible for the formation of the oxygenation product. However, such a reaction mechanism seems not applicable to the photoreaction system of $MOPDPP^+$ or $AcrH^+$. First, the Gibbs energy change of electron transfer from $MOPDPP^\bullet$ and $AcrH^\bullet$ to O_2 (to form $O_2^{\bullet-}$) is endergonic according to eq 3, where E°_{ox} and E°_{red} are the one-electron oxidation potential of $MOPDPP^\bullet$ or $AcrH^\bullet$ and the one-electron reduction potential of O_2. The reduction potential of $MOPDPP^+$ ($E_{red} = -0.42$ V vs SCE, Figure 5) [36]or $AcrH^+$ ($E_{red} = -0.43$ V vs SCE) is more positive than that of O_2 ($E_{red} = -0.87$ V vs SCE).[37] Thus, the electron

$$\Delta G^\circ_{et} = e\,(E^\circ_{ox} - E^\circ_{red}) \qquad (3)$$

is more positive than that of O_2 ($E_{red} = -0.87$ V vs SCE).[37] Thus, the electron transfer from $MOPDPP^\bullet$ and $AcrH^\bullet$ to O_2 should be little favored. Second, the LFP observations as described above indicated that the presence of O_2 had little effect on the lifetimes of $MOPDPP^\bullet$ and $AcrH^\bullet$ (Figures 2 and 3), suggesting no reaction occurs between the radicals and oxygen.

SCHEME 3



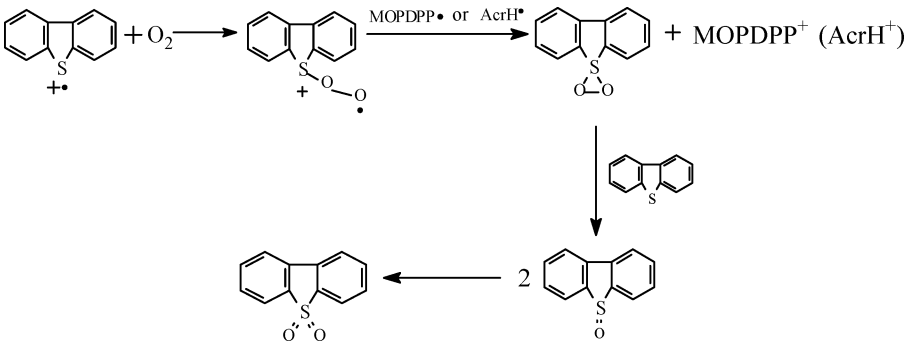
Finally, the ESR measurements also implied the lack of reactivity of $MOPDPP^\bullet$ and $AcrH^\bullet$ with oxygen. As shown in Figure 4, the ESR signals of $MOPDPP^\bullet$ and $AcrH^\bullet$ were increased (rather than decreased) when O_2 was introduced to the photoreaction system containing both DBT and $MOPDPP^+$ or $AcrH^+$ at 77 K. Such ESR observations suggested an alternative pathway for the reaction of molecular oxygen, forming an adduct with the DBT cationic radical (Scheme 2). This adduct will be responsible for subsequent oxygenation of the substrate compounds as discussed below.

In summary, the results discussed above show that it is very unlikely for O_2 to participate in the reaction process through the transient state of $^1O_2$ or $O_2^{\bullet-}$. Thus, the direct intermediate responsible for the oxygenation could not be formed via either the $^1O_2$ oxidation or the coupling of $O_2^{\bullet-}$ with DBT radical cation. It seems more reasonable to attribute the formation of the direct intermediate to the coupling reaction between DBT radical cation and the ground-state O_2. Such an assumption is in agreement with the ESR observation (Figure 4), in which the ESR signals of the radicals of $MOPDPP^\bullet$ and $AcrH^\bullet$ were enhanced in the presence of oxygen, due to the coupling of the DBT radical cation with O_2 and thus reducing the back ET from the photosensitizer radicals to DBT radical cation.

Taking into account the chemical characteristics of the persulfoxide and the fact that DBT sulfoxide was first formed during the photooxidation reaction, the electrophilic cylic thiadioxirane can reasonably be deemed to be the subsequent intermediate formed by the back electron transfer from the photosensitizer radicals to the persulfoxide species, accompanied by regeneration of $MOPDPP^+$ and $AcrH^+$, as shown in Scheme 2. The regeneration of sensitizer is also consistent with the fact that only small amount of sensitizer is needed for photooxidation of a larger amount of substrate compounds. The electrophilic cylic thiadioxirane oxidizes DBT to DBT sulfoxide, which is further oxidized to DBT sulfone.

Here, it should be noted that another possible intermediate, $MOPDPP-OO^\bullet$ and $AcrH-OO^\bullet$, which may be formed via the

SCHEME 2



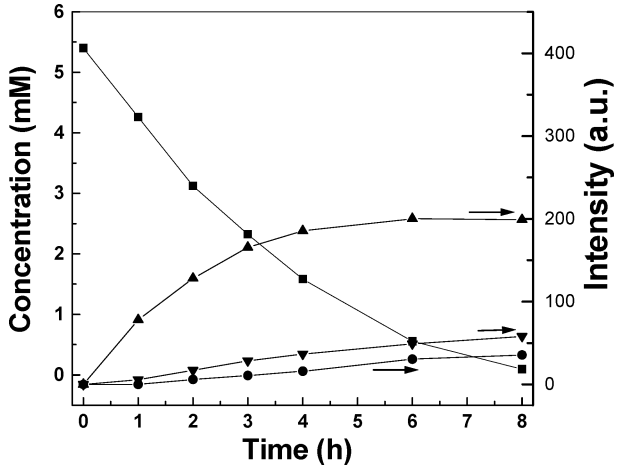
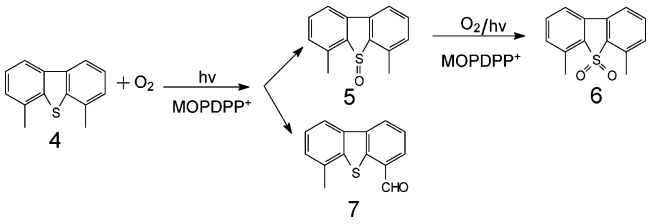


Figure 6. Changes in concentrations of DMDBT (■), DMDBT sulfoxide (▲), DMDBT sulfone (▼), compound 7 (●) vs irradiation time in the photooxidation of DMDBT (5.4×10^{-3} M) sensitized by MOPDPP$^+$ (4.3×10^{-4} M) in O_2-saturated acetonitrile solutions.

reaction of MOPDPP$^\bullet$ and AcrH$^\bullet$ with O_2,[38−40] is probably capable of oxidizing DBT.[41] But such a possibility could be discarded on the LFP and ESR results showing that negligible reactions of the photosensitizer radicals with O_2 were observed (Scheme 3).

Similar to the case of DBT, 4,6-dimethyldibenzothiophene (DMDBT) could also be efficiently oxidized, producing both corresponding sulfoxide and sulfone (Figure 6). The only difference is that a more compound **7** was formed (eq 4), which may be initiated by ET mechanism.[42]



Conclusions

Organic sulfides such as DBT and DMDBT have been effectively oxidized under visible irradiation in the presence of appropriate sensitizers such as MOPDPP$^+$. The selection of the specific substrate compounds rules out the oxidation pathway through singlet-oxygen, thus simplifying the reaction system for exploring the reaction mechanism. The LFP and ESR measurements indicated that the oxygenation reaction was initiated by the photoinduced ET between the excited sensitizer and the substrate compound, followed by the coupling of the DBT or DMDBT radical cation (thus formed) with O_2. The coupling reaction yields the intermediate adduct subject to further reaction to form the final oxygenated product. This finding provides a possibility for the photooxidation of sulfides with dioxygen utilizing visible light (solar energy).

Acknowledgment. Generous financial support by the Ministry of Science and Technology of China (no. 2003CB415006 and no.2002AA302303), by the National Science Foundation of China (no. 50436040, no. 20371048, no. 20520120221, no. 20277038, no. 50221001, and no. 20407016), by the Chinese Academy of Sciences and PetroChina Company Limited is gratefully acknowledged.

Supporting Information Available: The HPLC chromatogram of the photooxidation products of DBT (Figure S1), the photooxidation curve of DBT with molecular oxygen using AcrH$^+$ as the photosensitizer (Figure S2), the fluorescence spectra changes of MOPDPP$^+$ in the presence of DBT (Figure S3), Cyclic voltammogram of DBT in acetonitrile containing $Bu_4N^+PF_6$ (Figure S4), the fluorescence spectra changes of AcrH$^+$ in the presence of DBT (Figure S5), and the transient absorption spectra of the excited of MOPDPP$^+$ in both the absence and the presence of O_2 (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(42) When visible irradiation of the acetonitrile solution of MOPDPP$^+$ and *p*-xylene was under O_2-saturated conditions, the sole oxygenated product, *p*-tolualdehyde, was detected. The ESR signal of MOPDPP was also observed in *p*-xylene-MOPDPP$^+$ system as in the DBT− MOPDPP$^+$ system. Therefore, an ET mechanism was deemed to be working in the formation of compound.