NOTE

Requirement of Polar Organic Solvents for Photosensitized Oxidation of Dibenzothiophenes and Biphasic Photooxidative Desulfurization of Light Gas Oil

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Abstract : Photooxidation of dibenzothiophene in the presence of molecular oxygen and a photosensitizer like anthraquinone (AQ) proceeded in MeCN, AcOH, acetone and MeOH but not in benzene or n-octane, indicating the requirement of polar solvents. The addition of MeCN to nonpolar solvent initiated the AQ-sensitized photooxidation even when the solvent was biphasic as in an n-octane/MeCN mixture. The major oxidation product of dibenzothiophene was the corresponding sulfoxide. 4,6-Dimethyldibenzothiophene is a very unreactive sulfur compound during hydrodesulfurization but its photooxidation proceeds about 4 times faster than that of dibenzothiophene during the co-photooxidation. Sulfur content in light gas oil was reduced to below 10 ppm in the AQ-sensitized photooxidation in biphasic system consisting of light gas oil and MeCN.

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1 Introduction

Organic sulfur in light gas oil is usually removed by hydrodesulfurization. However, the remaining sulfur content is still high (about 500 ppm in Japan) even after deep desulfurization and is a major concern of the public. Because of steric hindrance, alkylated dibenzothiophenes substituted at 4 and/or 6 positions are the most difficult compounds to remove by hydrodesulfurization (1,2). A new method to remove alkylated dibenzothiophenes from light gas oil should thus be developed. For this purpose, oxidative desulfurization has received considerable attention in recent years. Peroxy-acids (3), hydrogen peroxide/phosphotungstic acid (4), and ozone (5) were used as

oxidants and photooxidation (6) was also considered. Shiraishi *et al.* reported that 9,10-dicyanoanthracene (DCA)-sensitized photooxidation of dibenzothiophenes proceeded smoothly in MeCN and their biphasic photooxidation system consisting of light gas oil and MeCN was effective for the reduction of sulfur content in light gas oil (7,8). Here we report anthraquinone (AQ) to be a very effective photosensitizer in the oxidation of dibenzothiophene **1a** and dimethyldibenzothiophene **1b**, the requirement of polar solvents for the AQ-sensitized photooxidation, and the usefulness of our photooxidation system for the removal of sulfur compounds from light gas oil.

2 Experimental

2.1 General

A 300-W xenon lamp (Hyper Xenon Exciter,

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Bunkoukeiki Co., Ltd.) was used as the irradiation source. ¹H NMR spectra were measured on a JEOL Lambda 500 (500 MHz) spectrometer. Mass spectra were obtained with a ThermoQuest Voyager GC-MS spectrometer by electron impact ionization at 70 eV. Oxidation products were characterized by GC-MS. Sulfur content of light gas oil was measured using an Antek 7000B analyzer. High-performance liquid chromatography (HPLC) analysis was carried out using a Shimadzu LC-10AD instrument with a SPD-10AD UV detector at 320 nm, on a Wakosil-II 5C18 RS column (4.6 × 150 mm) eluting with a linear gradient of MeCN/H₂O=30/70 to 90/10 (v/v) over 20 min at flow rate of 1.0 ml min⁻¹. Retention times for **1a**, **2a**, **3a**, **1b**, **2b**, **3b**, and AQ were 18.8, 6.9, 10.3, 22.6, 10.6, 13.9, and 14.5, respectively. Relative UV sensitivities at 320 nm of **2a**, **3a**, **1b**, **2b**, **3b**, and AQ to **1a** were 0.68, 0.84, 1.27, 1.13, 1.41, and 2.13, respectively. Commercially available compounds, **1a**, **3a**, and **1b**, and solvents were used without purification. Hydrodesulfurized light gas oil was from Japan Energy Co., Ltd.

2·2 General Procedure for Photosensitized Oxidation of Dibenzothiophenes

1a (185 mg, 1 mmol) and AQ (21 mg, 0.1 mmol) were dissolved in MeCN (100 mL). After purged with oxygen, the stirred solution was irradiated externally through Pyrex (λ > 280 nm) with a 300-W xenon lamp under a stream of oxygen at 20°C. Conversion of **1a** and yields of the products, **2a** and **3a**, were determined by HPLC.

2·3 Preparation of Dibenzothiophene 5-Oxide 2a

The preparation of **2a** from **1a** was carried out by the method of Watanabe *et al.* (9). ¹H NMR (CDCl₃) δ = 7.49 (dd, J=7.9, 8.1 Hz, 2H), 7.58 (dd, J=7.7, 8.1 Hz, 2H), 7.80 (d, J=7.7 Hz, 2H), 7.97 (d, J=7.9 Hz, 2H). MS m/z (rel intensity) 200 (M⁺; 87), 171 (100).

2·4 Preparation of 4,6-Dimethyldibenzothiophene 5-Oxide 2b

The same procedure as for **2a** was applied to **1b**. ¹H NMR (CDCl₃) δ = 2.75 (s, 6H), 7.23 (d, J=7.6 Hz, 2H), 7.47 (dd, J=7.6, 7.6 Hz, 2H), 7.60 (d, J=7.6 Hz, 2H). MS m/z (rel intensity) 228 (M⁺; 100).

2·5 Preparation of 4,6-Dimethyldibenzothiophene 5,5-Dioxide 3b

The preparation of **3b** from **1b** was performed by the method of McKillop *et al.* (10). ¹H NMR (CDCl₃) δ = 2.70 (s, 6H), 7.23 (d, J=7.6 Hz, 2H), 7.46 (dd, J=7.6, 7.6 Hz, 2H), 7.56 (d, J=7.6 Hz, 2H). MS m/z (rel intensity) 244 (M⁺; 100).

2·6 General Procedure for the Photooxidative Desulfurization of Light Gas Oil

Light gas oil (50 mL) was mixed with MeCN solution (50 mL) of AQ (42 mg, 0.2 mmol), but they were immiscible. After purged with oxygen, the stirred solution was irradiated externally through Pyrex with a 300-W xenon lamp under a stream of oxygen at 20°C for 2 h. The light gas oil phase was then separated, washed with water, dried over calcium chloride and filtered. The sulfur content in resulting oil was measured.

3 Results and Discussion

3·1 Photosensitized Oxidation of Dibenzothiophenes

The results of photosensitized oxidation of dibenzothiophenes are summarized in Table 1. **1a** in MeCN was photooxidized rapidly in the presence of AQ to afford the corresponding sulfoxide, dibenzothiophene 5-oxide **2a**, and the sulfone, dibenzothiophene 5,5-dioxide **3a** (Eq. 1). The photooxidation of **1a** failed to proceed in the absence of sensitizer or molecular oxygen (entries 2, 3). AQ was as effective as DCA (entries 4, 5). There was no loss of AQ during oxidation under our experimental conditions. In contrast, DCA gradually decomposed, suggesting that AQ is more desirable than DCA. 1,2-Naphthoquinone, 5, 12-naphthacenequinone, phthalic anhy-

Table 1 Photosensitized Oxidation of Dibenzothiophenes (10 mM)^a.

Entry	Substrate	Photosensitizer (1 mM)	Solvent	Conversion /mol%	Yield/mol%	
					Sulfoxide	Sulfone
1	1a	AQ	MeCN	95	65 (2a)	13 (3a)
2		—	MeCN	0	—	—
3		AQ	MeCN ^b	0	—	—
4		AQ (0.5 mM)	MeCN	90	71	11
5		DCA (0.5 mM)	MeCN	96	75	13
6		1,2-Naphthoquinone (0.5 mM)	MeCN	10	8	0
7		5,12-Naphthacenequinone (0.5 mM)	MeCN	11	10	0
8		Phthalic anhydride (10 mM)	MeCN	29	28	1
9		Maleic anhydride (10 mM)	MeCN	25	24	1
10		1,4-Benzoquinone (2 mM)	MeCN	0	—	—
11		Benzophenone (2 mM)	MeCN	0	—	—
12		Succinic anhydride (10 mM)	MeCN	0	—	—
13		AQ	AcOH	87	76	1
14		AQ	Acetone	73	65	5
15		AQ	MeOH	40	37	0
16		AQ	Benzene	0	—	—
17		AQ	Benzene/MeCN ^c	56	50	2
18		AQ (about 0.5 mM) ^d	n-Octane	0	—	—
19		AQ (1.8 mM in MeCN)	n-Octane/MeCN ^{c,e}	83	73	7
20	1b	AQ	MeCN	87	57 (2b)	10 (3b)

^a Irradiated externally through Pyrex with a 300-W xenon lamp under oxygen for 60 min at 20°C. ^b Under nitrogen.^c 50:50 v/v. ^d Solution saturated with AQ. ^e n-Octane and MeCN are immiscible under this condition.

dride and maleic anhydride also served as sensitizers (entries 6~9), but were much less effective than AQ. The corresponding free acids, esters and imides of the above acid anhydrides also worked as sensitizers, but were less effective than the acid anhydrides (data not shown). 1,4-Benzoquinone, benzophenone and succinic anhydride did not work as sensitizers under our experimental conditions (entries 10~12). AQ-sensitized photooxidation of **1b**, a very unreactive sulfur compound during hydrodesulfurization (1, 2), in MeCN also proceeded smoothly (entry 20). Moreover, **1b** was consumed about 4 times faster than **1a** in co-photooxidation of 10 mM each of the two compounds, suggesting that this photooxidation system is very useful for removing dimethyldibenzothiophenes from light gas oil.

A plausible mechanism for the photooxidation of **1a** is shown in **Scheme 1** which is similar to that proposed for AQ (11) and DCA (7, 8, 12~14). First, photosensitizer (PS) is converted to the photoexcited form (PS*). The reaction of PS* with **1a** gives radical anion (PS^{•-}) and the radical cation **1a**^{•+}. PS^{•-} converts oxygen to superoxide (O₂^{•-}) and reaction of **1a**^{•+} with O₂^{•-} gives a persulfoxide intermediate which finally oxidize **1a** to **2a**. Higher yields of sulfoxides than sulfones (**Table 1**) supports this

mechanism. Sulfones are likely produced from persulfoxide intermediate (15, 16).

Photooxidation of **1a** proceeded not only in MeCN but also in other polar solvents such as AcOH, acetone and MeOH (entries 13~15). AQ decayed in MeOH (17) but not in MeCN, indicating that MeCN is more appropriate than MeOH.

AQ-sensitized photooxidation of **1a** did not proceed in nonpolar solvents such as benzene or n-octane (entries 16, 18). However, the addition of MeCN to benzene initiated the AQ-sensitized photooxidation of **1a** (entry 17). n-Octane and MeCN are immiscible, but the addition of MeCN to n-octane also initiated the AQ-induced photooxidation of **1a** (entry 19). We confirmed that 57% of **1a** and 85% of AQ are present in MeCN phase in our experimental conditions and this should be advantageous for the oxidation of **1a** since photooxidation proceeds only in MeCN phase. We also found that 98% of **2a** is present in MeCN phase, suggesting that oxidation products is mostly transferred into MeCN phase.

3.2 Photooxidative Desulfurization of Light Gas Oil

We next applied this biphasic photooxidation system to light gas oil. The results are summarized in **Table 2**. We used deep hydrodesulfurized light gas oil

Scheme 1

containing 362 ppm of sulfur. Small reduction in sulfur content was observed without irradiation (entry 23) since organic sulfur in light gas oil migrates to the MeCN phase. Five consecutive extractions with MeCN reduced sulfur content in light gas oil only to 243 ppm, indicating extraction alone not to be sufficient. AQ-photosensitized oxidation of light gas oil for 4 hours reduced sulfur content remarkably to 81 ppm (entry 21). Increase in MeCN volume and AQ concentration accelerated the removal of the sulfur by 59 and 28 ppm, respectively (entries 24 and 25). DCA was effective in the present system (entry 26) as expected from previous reports (7, 8). However, AQ

is more practical than DCA since AQ is much less expensive. Replacement of the AQ-containing MeCN during irradiation was very successful and we could reduce sulfur content in light gas oil to as little as 6 ppm (entry 28).

4 Conclusion

AQ is an effective photosensitizer for the oxidation of dibenzothiophenes in polar organic solvents. The AQ-sensitized photooxidation in biphasic system consisting of light gas oil and MeCN is useful for removing sulfur compounds from light gas oil.

Table 2 Photooxidative Desulfurization of Light Gas Oil^{a,b}.

Entry	Photoirradiation	Photosensitizer Name	Amount/mmol	Light gas oil:MeCN /ml/ml	Sulfur content /ppm
21	Yes	AQ	0.1	50/50	81
22	Yes	—	—	50/50	208
23	No	—	—	50/50	303
24	Yes	AQ	0.1	50/200	59
25	Yes	AQ	0.4	50/200	28
26	Yes	DCA	0.1	50/200	14
27	Yes	AQ	0.1 × 2 ^c	50/(200 × 2) ^c	18
28	Yes	AQ	0.4 × 2 ^c	50/(200 × 2) ^c	6

^a Irradiated externally through Pyrex with a 300-W xenon lamp under oxygen for 4 hours at 20°C. ^b Sulfur content of light gas oil was 362 ppm. ^c MeCN phase was replaced by new MeCN solution of AQ after 2 hour irradiation and irradiated for 2 hours.

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