Ind. Eng. Chem. Res. **1998,** *37,* 203−211

A Deep Desulfurization Process for Light Oil by Photochemical Reaction in an Organic Two-Phase Liquid−Liquid Extraction System

Yasuhiro Shiraishi,[†] Takayuki Hirai,*,[†] and Isao Komasawa[†,‡]

Department of Chemical Science and Engineering, Graduate School of Engineering Science, Osaka University, Machikaneyama-cho 1-3, Toyonaka, Osaka 560, Japan, and Research Center for Photoenergetics of Organic Materials, Osaka University, Machikaneyama-cho 1-3, Toyonaka, Osaka 560, Japan

A novel deep desulfurization process of light oil, effected by a combination of photochemical reaction and organic two-phase liquid−liquid extraction, has been investigated. The process is comprised of two stages. The first consists of the transfer of the sulfur-containing compounds from the light oil to an aqueous-soluble polar solvent. This is then followed by the photooxidation and photodecomposition of the sulfur-containing compounds in the solvent by UV irradiation, using a high-pressure mercury lamp. The operations are carried out under conditions of room temperature and atmospheric pressure. Acetonitrile was found to be the most suitable polar solvent for the process. In acetonitrile, dibenzothiophene (DBT) is converted to DBT 5-monoxide and then to DBT 5,5-dioxide, dibenz[*c*,*e*][1,2]oxathiin 6-oxide, and aromatic sulfonate or sulfinate anion by the UV irradiation. These products are highly polarized and are therefore not distributed into the nonpolar light oil phase. An adverse effect of naphthalene, in depressing the photodecomposition of DBT, is actually reduced by the use of an acetonitrile solution. The desulfurization yield for commercial light oil (CLO) and for straight-run light gas oil (LGO) is drastically improved by the present process, the sulfur content of CLO being reduced from 0.2 to 0.05 wt % by 2 h of irradiation and that of LGO from 1.4 to 0.05 wt % by 10 h of irradiation. The separation of the coextracted aromatics from the acetonitrile was carried out successfully by using light paraffinic hydrocarbon stripping agents.

Introduction

Air pollution, caused by diesel exhaust gas (SO*x*), is one of the most serious problems in the world, and much attention has been focused on the deep desulfurization of light oil. Sulfur-containing compounds are also undesirable in the refining processes because they tend to deactivate various catalysts used in downstream processing and in the upgrading of hydrocarbons. A catalytic hydrodesulfurization (HDS) method is employed industrially but requires both high hydrogen pressures and high temperatures, and to produce deep-desulfurized fuels, the demand for hydrogen will inevitably increase. In addition, the HDS method has difficulty in the desulfurization of dibenzothiophene (DBT) and its derivatives among sulfur-containing compounds in light oil (Kabe *et al.*, 1992).

A novel desulfurization process for DBTs by photochemical reaction and liquid−liquid extraction using an organic/water two-phase system has been proposed in previous papers (Hirai *et al.*, 1996), and this has been extended for benzothiophenes (BTs) and alkyl sulfides (Hirai *et al.*, 1997a). DBTs, in a tetradecane solution, were found to be photodecomposed by the use of a high-pressure mercury lamp and were removed into the water phase as a sulfate anion. The previous study, however, revealed the problem that the removal of DBTs from tetradecane is depressed markedly by the presence of naphthalene and that this is caused by triplet energy transfer from the photoexcited DBT to the ground-state naphthalene. This may be a serious problem for the desulfurization of light oil, since light oil contains two-ring aromatic compounds such as naphthalene and its derivatives having a lower triplet energy. The desulfurization was improved by introducing a triplet photosensitizer into the light oil and hydrogen peroxide into the water phase (Hirai *et al.*, 1997b). Hydrogen peroxide was found to be effective, since it acts as a weak oxidizing agent for the photoexcited DBT and to some extent interrupts the energy transfer from the excited DBT to the naphthalene. In these previous studies, the basic idea for desulfurization was that of the photodecomposition of sulfur-containing compounds in the light oil phase, followed by the transfer of the resultant decomposed compounds into the aqueous phase. Thus, deactivation of the photoexcited DBTs by naphthalene appeared, more or less, inevitable.

In the present work, a different extraction and photoreaction system, utilizing the polarity difference between the sulfur-containing compounds such as DBT and the aliphatic components of light oil, is employed. Here the idea is to transfer the sulfur-containing compounds to the other phase and then to photooxidize and decompose them there. Polar solvents, immiscible with the feed oil phase, can be employed as the extraction phase to form an organic two-phase liquid−liquid system. BTs and DBTs have a relatively large polarity and therefore tend to transfer into the polar solvent, together with other aromatic compounds. This organic two-phase system, combined with photochemical reac-

---

* Author to whom correspondence is addressed. E-mail: hirai@cheng.es.osaka-u.ac.jp. Fax: +81-6-850-6273. Telephone: +81-6-850-6272.

[†] Department of Chemical Science and Engineering.

[‡] Research Center for Photoenergetics of Organic Materials.

S0888-5885(97)00388-6 CCC: $15.00

Table 1. Aromatic and Sulfur Contents of Commercial Light Oil (CLO) before and after Contact with Polar Solvents

		after contact with								
		DMSO			sulfolane			acetonitrile		
solvent/CLO volume ratio	before contact (feed)	1	3	7	1	3	7	1	3	7
saturated hydrocarbon (vol %)	76.2	77.3	78.7	80.6	77.9	79.6	81.8	79.2	82.0	85.4
one-ring aromatics (vol %)	19.5	19.0	18.2	17.0	18.8	17.7	16.2	17.6	15.5	12.9
two-ring aromatics (vol %)	4.3	3.7	3.1	2.4	3.3	2.7	2.0	3.2	2.5	1.7
total sulfur content (wt %)	0.1896	0.1785	0.1644	0.1550	0.1744	0.1511	0.1226	0.1638	0.1322	0.1047

tion, is then the basis for this study of the deep desulfurization of light oil.

Experimental Section

Materials. Dibenzothiophene (DBT), benzothiophene (BT), naphthalene, tetradecane (n-$C_{14}H_{30}$), dimethyl sulfoxide (DMSO), tetramethylene sulfone (sulfolane), biphenyl, 2-propanol, and acetonitrile were supplied by Wako Pure Chemical Industries, Ltd., and were used without further purification. Dibenzothiophene 5-monoxide (DBT-O) and dibenzothiophene 5,5-dioxide (DBT-O_2) were synthesized from DBT using the H_2O_2−AcOH oxidation procedure (Gilman and Esmay, 1952). 4-Methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were prepared as reported by Gerdil and Lucken (1965). Dibenz[*c*,*e*][1,2]oxathiin 6-oxide (DBT sultine) was prepared by the methods of Hanson and Kemp (1981).

Apparatus and Procedure. The commercial light oil (CLO) and straight-run light gas oil (LGO) were mixed vigorously using a magnetic stirrer with a polar solvent solution in the volume ratio from 50/350 to 200/200 mL/mL with a total solution volume of 400 mL. The solutions were photoirradiated by immersing a high-pressure mercury lamp (300 W; Eikohsha Co., Ltd., Osaka, Japan), combined with air bubbling at atmospheric pressure. The DBT/solvent and BT/acetonitrile (400 mL) homogeneous solutions were also employed for photoreaction studies, combined with stirring. The extent of photoreaction for DBT was found to be little affected by bubbling rate in the range of 300−1500 mL/min, as in the case of direct photoreaction of DBT in light oil (Hirai *et al.*, 1996), and therefore the bubbling rate of 500 mL/min was adopted in all runs. Pyrex and uranil glass filters were used to give light wavelength rejections of less than 280 and 320 nm, respectively. The temperature of the solutions was about 323 K during photoirradiation, and the photoreactor was equipped with a reflux condenser to minimize the loss of solvent by evaporation.

Analysis. The DBT and naphthalene concentrations in tetradecane were analyzed by gas chromatography (Shimadzu GC-14B equipped with FID). The DBT, DBT-O, DBT-O_2, and DBT sultine concentrations in acetonitrile, acetonitrile−water mixture, and polar solvent solutions were analyzed by reverse-phase HPLC (Shimadzu LC-6A equipped with a spectrophotometric detector SPD-6A) and by gas chromatography with on-column injections (Vignier *et al.*, 1983). GC−MS analyses were carried out on a JEOL JMS-DX303HF mass spectrophotometer. The total saturated hydrocarbon and one- and two-ring aromatic hydrocarbon contents in light oil were analyzed by normal-phase HPLC (Shimadzu LC-6A equipped with a refractive index detector RID-6A), using the sensibility correction method (JPI-5S-49-97). The total sulfur concentration in light oil was measured by the inductively coupled argon plasma atomic emission spectrophotometer (Nippon Jarrell-Ash ICAP-575 Mark II) and by oxidative microcoulometry (ASTM D 3120). The sulfur-containing compounds in light oil were analyzed by gas chromatography−atomic emission detector (GC−AED; Hewlett Packard 5890 equipped with AED 5921A).

Results and Discussion

Liquid−Liquid Extraction of Sulfur-Containing Compounds. The extractability of the sulfur-containing compounds and aromatic hydrocarbons from light oil was studied by contacting commercial light oil (CLO), with acetonitrile, dimethyl sulfoxide (DMSO), and tetramethylene sulfone (sulfolane) at room temperature conditions. The latter two solvents are the normal solvents used for aromatics extraction in the petroleum industry (Bailes, 1983). Extraction equilibrium between CLO and a polar solvent was achieved in 5 min or less, and the phase separation was achieved in about 10 s. The light oil was washed once with an equal volume of water to remove the dissolved polar solvents, prior to analysis. Table 1 shows a comparison of the sulfur and aromatics content of the feed and treated CLO as a function of the solvent/CLO volume ratio. In these experiments, acetonitrile is shown to be the most effective solvent for the extraction of the sulfur-containing compounds. Similar results were obtained also for straight-run light gas oil (LGO). Thus, acetonitrile is considered to be the most suitable solvent for light distillates.

Table 2 shows the effect of liquid−liquid extraction, using acetonitrile as solvent (acetonitrile/CLO and LGO volume ratio = 3), on the composition of the sulfur-containing compounds in CLO and LGO, as obtained by GC−AED analysis. Using single contact with acetonitrile, 47% of the BTs and 36% of the DBTs in CLO and 39% of the BTs and 24% of DBTs in LGO were removed. The BTs were transferred more to the acetonitrile phase than the DBTs due to their higher polarity. Figure 1 shows the effect of the carbon number of alkyl substituents on the distribution of BTs and DBTs. The remaining portion has a tendency to increase with an increase in the carbon number of the alkyl substituents. This indicates that distribution into the acetonitrile phase is reduced with the carbon number. The interaction between the acetonitrile solvent and π-electron on BTs and DBTs is considered to be sterically blocked by the alkyl substituent, as in the case of aromatic extraction with the DMSO solvent (Natusch and Tomkins, 1978).

Photoreaction of DBT in Polar Solvents. Figure 2 shows the time-course variation in the concentrations of DBT during photoirradiation, when dissolved in various solvents. In protic solvents such as 2-propanol and methanol, DBT was hardly photodecomposed. In acetonitrile, however, DBT was easily photodecomposed and was quantitatively decomposed by 5 h of photoir-

Table 2. Effect of Liquid−Liquid Extraction with Acetonitrile (Acetonitrile/Commercial Light Oil (CLO) and Acetonitrile/Straight-Run Light Gas Oil (LGO) Volume Ratio = 3) and of 2 h of Photoirradiation on the Composition of Sulfur-Containing Compounds in CLO and in LGO

	CLO			LGO		
carbon number of substituent	feed (wt %)	after extraction (wt %)	with photoirradiation (wt %)	feed (wt %)	after extraction (wt %)	with photoirradiation (wt %)
<C1-BT	0.0019	0.0009	0.0002	0.0157	0.0079	0.0024
C2-BT	0.0072	0.0028	0.0006	0.0315	0.0143	0.0055
C3-BT	0.0126	0.0056	0.0016	0.1173	0.0612	0.0215
C4-BT	0.0101	0.0060	0.0025	0.1336	0.0787	0.0279
C5-BT	0.0057	0.0032	0.0011	0.0850	0.0534	0.0195
C6-BT	0.0081	0.0052	0.0019	0.1362	0.0953	0.0356
C7-BT	0.0008	0.0005	0.0002	0.0110	0.0093	0.0033
C8-BT	0.0024	0.0017	0.0007	0.0295	0.0237	0.0088
BTs (total)	0.0488	0.0259	0.0088	0.5598	0.3438	0.1245
DBT	0.0034	0.0015	0.0010	0.0373	0.0214	0.0098
4-MDBT	0.0057	0.0024	0.0013	0.0337	0.0192	0.0105
C1-DBT	0.0056	0.0029	0.0014	0.0657	0.0412	0.0201
4,6-DMDBT	0.0066	0.0032	0.0019	0.0265	0.0179	0.0094
C2-DBT	0.0164	0.0089	0.0047	0.1282	0.0852	0.0455
C3-DBT	0.0239	0.0143	0.0083	0.1514	0.1123	0.0597
C4-DBT	0.0151	0.0098	0.0059	0.0981	0.0763	0.0423
C5-DBT	0.0041	0.0028	0.0017	0.0270	0.0215	0.0124
C6-DBT	0.0504	0.0383	0.0240	0.2723	0.2412	0.1658
DBTs (total)	0.1312	0.0841	0.0502	0.8402	0.6362	0.3755
total sulfur content	0.1800	0.1100	0.0590	1.4000	0.9800	0.5000

radiation. The photodecomposition rate for DBT in acetonitrile was 5-fold higher than that in tetradecane, such that DBT appears to photoreact effectively in aprotic solvents. The photoreactivity of DBT in sulfolane and DMSO was, however, less than that in tetradecane. These sulfur-containing solvents have a broad absorption band, starting from 250 nm, and thus DBT in these solvents cannot absorb the UV light sufficiently for excitation. Acetonitrile hardly absorbs UV light in the range 200−300 nm, thus allowing the photoreaction of DBT. Thus, acetonitrile is regarded to be the most suitable solvent for the photoreaction of DBT.

Figure 3 shows the time-course variation in the concentrations of DBT in tetradecane and acetonitrile in the presence of naphthalene. DBT in tetradecane is hardly photodecomposed. This is because of the energy transfer from the excited-state DBT to the ground-state naphthalene, as encountered in the previous study (Hirai *et al.*, 1997b). In acetonitrile, although the decomposition rate is slightly decreased by an increase in the concentration of naphthalene, DBT was nevertheless still photodecomposed satisfactorily in the presence of naphthalene. The energy transfer from the excited DBT to naphthalene is likely to be suppressed in acetonitrile.

Mechanism of Photoreaction of DBT in Acetonitrile. Figure 4 shows the reverse-phase liquid chromatogram for HPLC analysis, obtained by monitoring at 241 nm, for the samples obtained by 4 h of photoirradiation of the DBT/acetonitrile ($[\mathrm{DBT}]_{\mathrm{initial}} = 27$ mM) homogeneous solution. Here, 75% of the initial DBT disappeared. With decreasing DBT concentration, new peaks were eluted at around 3, 5−6, and 8 min. These peaks were confirmed to be attributable to DBT 5-monoxide (DBT-O), DBT 5,5-dioxide (DBT-O_2), and dibenz[*c*,*e*][1,2]oxathiin 6-oxide (DBT sultine) by comparison of the retention times and by GC−MS analysis (Vignier *et al.*, 1983; Hanson and Kemp, 1981) with standard materials. Sulfoxide, sulfone, and sultine were eluted at earlier retention times than the parent DBT, due to their higher polarity.

Figure 5 shows the time-course variation in the DBT, DBT-O, DBT-O_2, and DBT sultine concentrations. DBT-O appeared at first, associated with the disappearance of DBT, but then decreased, with DBT-O_2 and DBT sultine then appearing with the later progress of irradiation. The DBT sultine concentration decreased with irradiation time, as with DBT-O. The sum of the quantities of DBT, DBT-O, DBT-O_2, and DBT sultine, however, was not equal to the amount of DBT in the initial feed, with the deviation becoming more apparent with increasing irradiation time, as shown by the broken line in Figure 5. The solution turned yellow with photoirradiation, and a large peak a in Figure 4, coeluted with the mobile phase, became greater with the progress of the reaction. These indicate that other products are also produced during the photoirradiation of DBT. When DBT-O_2 dissolved in acetonitrile was UV irradiated, the dioxide was not photodecomposed and the peak a was not detected. DBT-O has been found to be nonphotostable even at 77 K in EPA glass (Jenks *et al.*, 1994a), and also DBT-O_2 is essentially photoinert in solvents such as benzene and acetonitorile which are poor hydrogen atom donors, as reported by Jenks *et al.* (1994b). These findings support that other compounds are possibly produced via the photodecomposition of DBT-O.

In order to characterize the unidentified photodecomposed products, the sample obtained by 4 h of photoirradiation of the DBT/acetonitrile solution was eluted isocratically by 30 vol % of acetonitrile in water with different pH values. Figure 6 shows the reverse-phase liquid chromatograms for the irradiation products, when monitoring at 340 nm. These major peaks are separated more clearly and are retarded by a decreasing pH of the eluent, thus indicating that the compounds are anionic (e.g., sulfinate anion or sulfonate anion). Khudayer (1990) has reported that DBT was transformed to dibenzofuran by photolysis in an aqueous solution and

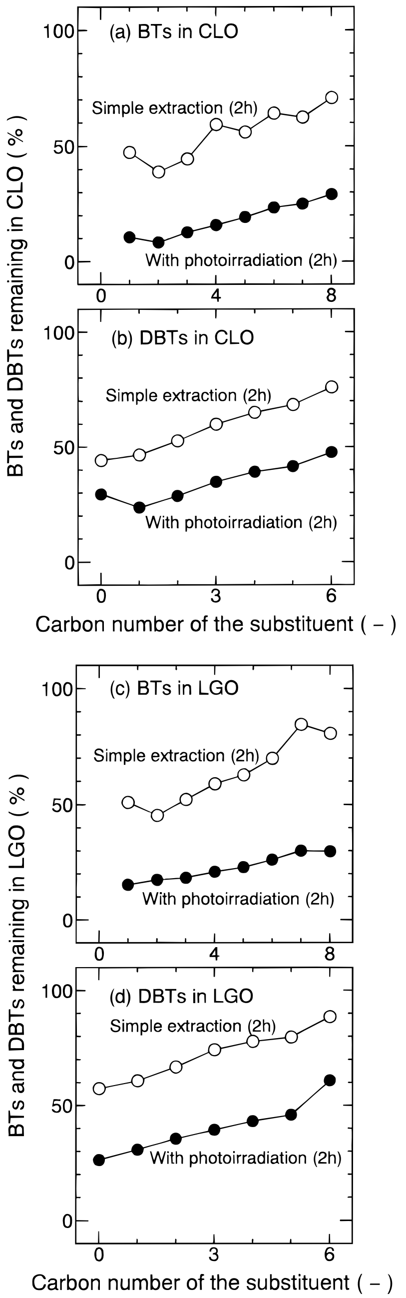

Figure 1. Remaining percent of sulfur-containing compounds in the light oils after contact with acetonitrile for 2 h with and without photoirradiation, with respect to the carbon number of the alkyl substituent. Acetonitrile/commercial light oil (CLO) or straight-run light gas oil (LGO) volume ratio = 3. The initial amount of each alkyl-substituted compound in the light oil is set as 100%.

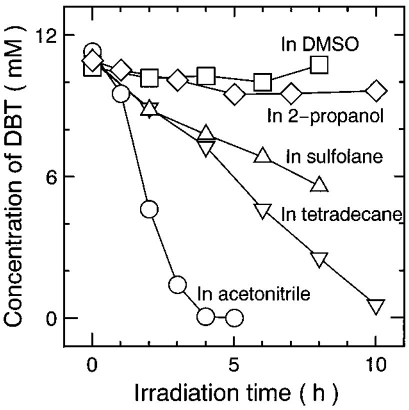

Figure 2. Time-course variation in the concentrations of DBT dissolved in various solvents, during photoirradiation.

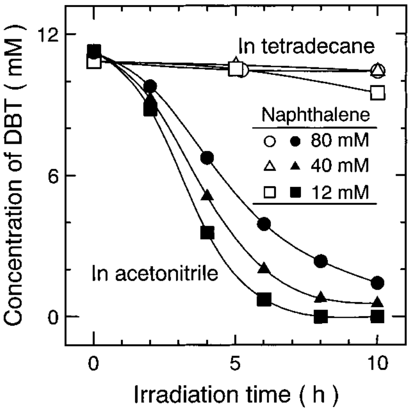

Figure 3. Time-course variation in the concentrations of DBT in tetradecane (open symbols) and acetonitrile (closed symbols) with various initial naphthalene concentrations.

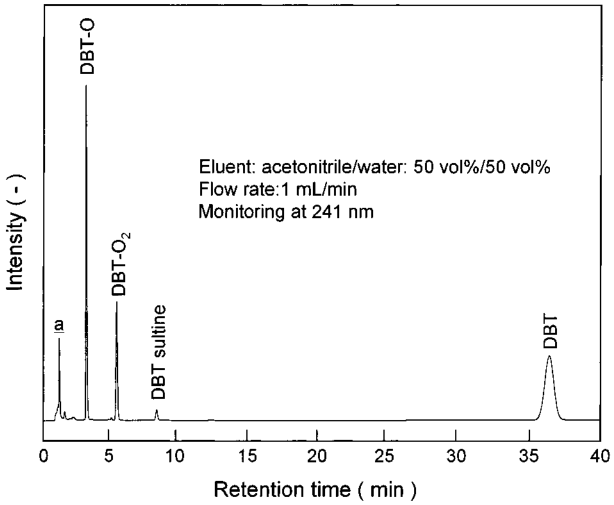

Figure 4. Reverse-phase liquid chromatogram for HPLC analysis, obtained by monitoring at 241 nm, for the samples obtained by 4 h of photoirradiation of the DBT/acetonitrile ($[DBT]_{initial}$ = 27 mM) solution.

in the presence of sodium salt. In the present case, biphenyl and dibenzofuran were, however, not detected by HPLC analysis. The eluting compounds showed a broad absorption at around 340 nm, and it was confirmed also by ion chromatographic analysis that SO_4^{2-}, SO_3^{2-}, and benzene sulfonate and sulfinate anions were not produced. These findings indicate that the unknown compounds are likely to consist of two-ring aromatic compounds, conjugated with substituent sulfinate or sulfonate anion. These results, together with the fact that $DBT-O_2$, DBT sultine, and the anionic compounds were observed when DBT-O/acetonitrile was photoirradiated, suggest that DBT is photooxidized to DBT-O and then to $DBT-O_2$ and that the reaction is actually accompanied by C−S cleavage (Chatgilialoglu *et al.*, 1980) of DBT-O to form DBT sultine and anionic compounds.

The photodecomposition products of DBTs in acetonitrile are unlikely to be distributed in nonpolar or nearly nonpolar solvents. To confirm this, the photoirradiated DBT/acetonitrile solution was contacted with 10-fold volumes of *n*-hexane. The peaks attributed to the photooxidized and photodecomposed compounds

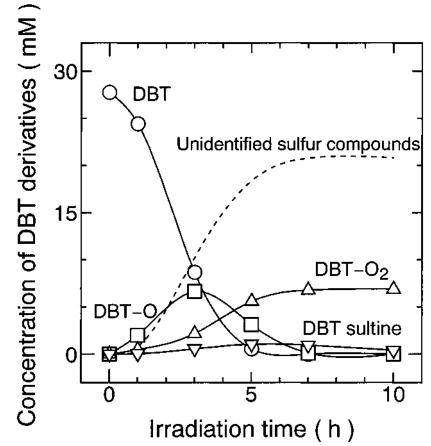

Figure 5. Time-course variation in the DBT, DBT-O, DBT-O$_2$, and DBT sultine concentrations in acetonitrile by photoirradiation ($[DBT]_{initial}$ = 27 mM).

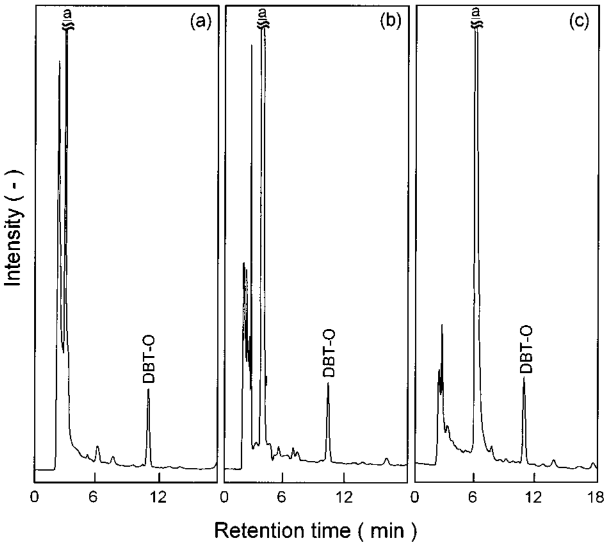

Figure 6. Reverse-phase liquid chromatograms for HPLC analysis, obtained by monitoring at 340 nm, for the sample obtained by 4 h of photoirradiation of the DBT/acetonitrile ($[DBT]_{initial}$ = 27 mM) solution, eluted isocratically by a 30% acetonitrile in water solution. pH: (a) 6.86 (phosphate buffer), (b) 4.01 (phthalate buffer) (c) 1.88 (KH_2PO_4, 5 mM; $HClO_4$, 0.1%).

were not changed by the treatment. This indicates that these compounds are more polar than the parent DBTs, confirming the report of Zannikos *et al.* (1995). DBT was converted to compounds which exist only in the acetonitrile phase.

Photoreactivity of DBT Derivatives and BT. Figure 7 shows the effect of the irradiative wavelength on the time-course variation in the DBT, DBT-O, DBT-O$_2$, and DBT sultine concentrations in an acetonitrile solution. In the case of a Pyrex filter ($\lambda > 280$ nm), the DBT was photodecomposed just as effectively as without the filter, although the formation of DBT-O$_2$, DBT sultine, and the unidentified anionic sulfur compounds was depressed. Using the uranil filter ($\lambda > 320$ nm), only DBT-O was formed, but with a lower DBT oxidation rate. In this case, the sequential reaction (photooxidation and C–S cleavage) via DBT-O hardly occurred, owing to the rejection of the short-wavelength light. In the range of wavelength for $\lambda > 320$ nm, direct excitation of the DBT hardly occurred, since the singlet excitation energy of DBT is known to be at 325.9 nm (367 kJ/mol) (Murov *et al.*, 1993). Thus, in this case, the photoreaction may occur upon irradiation of the CCT (contact charge transfer) band with UV–visible light (300–400 nm), as reported by Akasaka *et al.* (1987) and Tezuka *et al.* (1978).

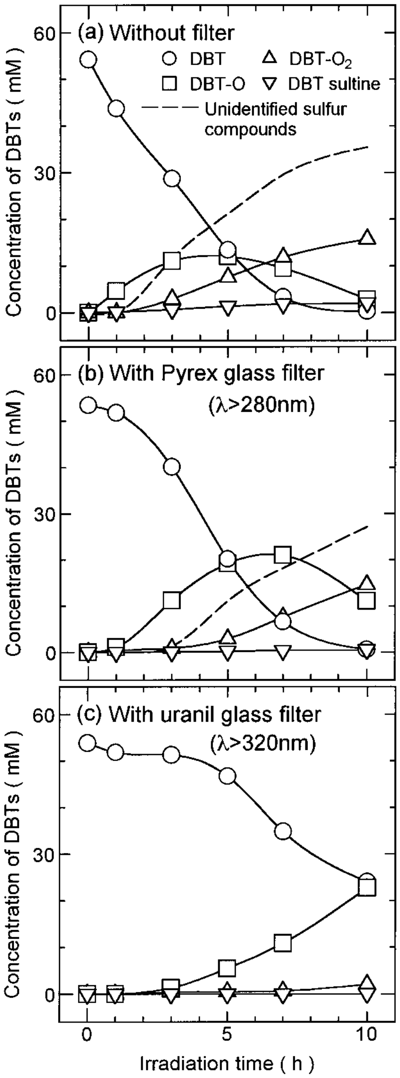

Figure 7. Effect of irradiative wavelength on time-course variation in the DBT ($[DBT]_{initial}$ = 54 mM), DBT-O, DBT-O$_2$, and DBT sultine concentrations in acetonitrile: (a) without filter; (b) with Pyrex glass filter ($\lambda > 280$ nm); (c) with uranil glass filter ($\lambda > 320$ nm).

Substituted DBTs and BTs are the main components of the sulfur-containing compounds in light oil. The photoreactivity of 4-MDBT and 4,6-DMDBT was, therefore, also studied and in acetonitrile the reactivity of these substituted DBTs was found to be higher than that of DBT, as shown in Figure 8. Thus, the order of reactivity is DBT < 4-MDBT < 4,6-DMDBT. This is the same order as that obtained for the removal of DBTs, in the tetradecane/water two-phase system (Hirai *et al.*, 1996). It was confirmed that 4-MDBT and 4,6-DMDBT were also converted to sulfoxide, sulfone, sultine, and anionic compounds by HPLC analysis, and the comparison of the retention time of the corresponding peaks is shown in Table 3.

The photoreactivity of BT was also studied. As shown in Figure 8, the BT reactivity was found to be higher than that of DBT, as for the tetradecane/water two-phase system (Hirai *et al.*, 1997a). The photodecomposition of BT in acetonitrile was also more rapid than in

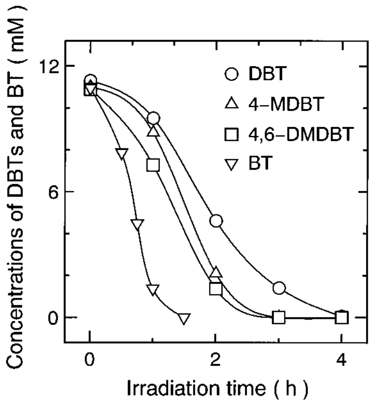

Figure 8. Comparison of the photodecomposition rate of DBT, its alkyl-substituted derivatives, and BT in acetonitrile.

Table 3. Retention Index of the Photodecomposed Products of DBT, 4-MDBT, and 4,6-DMDBT by the Analysis of HPLC[a]

	retention time (min)		retention time (min)
DBT	34.1	DBT-O$_2$	5.05
DBT-O	3.03	DBT sultine	7.82
4-MDBT	59.0	4-MDBT-O$_2$	7.04
4-MDBT-O	3.81	4-MDBT sultine	10.1
4,6-DMDBT	99.6	4,6-DMDBT-O$_2$	9.56
4,6-DMDBT-O	4.98	4,6-DMDBT sultine	16.1
BT	14.7		

[a] Mobile phase: acetonitrile/water = 50/50 vol %. Flow rate: 1.0 mL/min. Column temperature: 293 K.

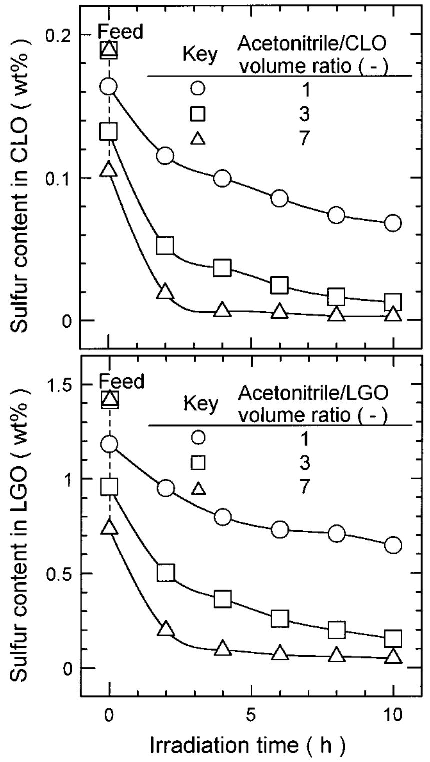

Figure 9. Time-course variation in the sulfur contents in (a) commercial light oil (CLO) and (b) straight-run light gas oil (LGO) using an organic two-phase system, combined with photoirradiation.

the tetradecane/water two-phase system. As with DBT, a peak co-eluted with the mobile phase was shown by HPLC analysis, showing that BT was also photoconverted by UV irradiation to more polarized compounds.

Desulfurization of Light Oil Using an Organic Two-Phase Liquid–Liquid Extraction System. Liquid–liquid extraction using an organic two-phase system, combined with photoreaction, was employed. The effect of 2 h of photoirradiation on the variation of the composition of sulfur-containing compounds is shown in Table 2. When the data are plotted against the carbon number of the alkyl substituents as shown in Figure 1, the results of the remaining percent after 2 h of photoirradiation show nearly parallel lines with those obtained without photoirradiation. This means that the photoreactivities of compounds with different carbon numbers are not very much different from each other. The total sulfur contents in the solutions are, thus, considered hereafter.

Figure 9 shows variations in the sulfur contents of CLO and LGO with respect to irradiation time, as a function of the oil/solvent phase volume ratio. The data at an irradiation time of zero are those obtained simply by mixing the two phases and show the distribution equilibria for the sulfur contents in the organic two-phase system. In combination with photoirradiation, the desulfurization yield is shown to be much enhanced. At the higher acetonitrile/CLO phase volume ratio of 7, the sulfur content was found to be decreased from 0.2 to 0.02 wt % by only 2 h of photoirradiation and to less than 0.005 wt % by 4 h of photoirradiation. In the case of LGO, simple contact with acetonitrile without photoirradiation reduced the sulfur content from 1.4 to 0.7 wt %. The sulfur content of LGO was decreased to 0.2 wt % by 2 h of photoirradiation and to less than 0.05 wt % by 10 h of photoirradiation. For LGO, the desulfurization rate for the time period 0–2 h was 6-fold higher than that for CLO. LGO contains a large quantity of BT and its associated derivatives (0.56 wt %); hence, it is much more easily photodecomposed, and leads to a greater apparent desulfurization rate for LGO than for CLO.

The values for the sulfur distribution ratio, D_s, defined as the ratio of the total sulfur content in the acetonitrile and in light oil, are shown in Figure 10. Although as expected, the values of D_s for both feeds are hardly changed by the volume ratio without photoirradiation, the ratios increased with increasing volume ratio, when irradiation was applied. At a volume ratio of 7, the values of D_s are increased 11-fold in CLO and 9-fold in LGO as compared to that with no photoirradiation. This indicates that the photoreaction of BTs and DBTs in acetonitrile proceeds more effectively with an increasing volume ratio of acetonitrile. This may be caused by a decrease in the photoscattering and light exclusion by the light oil phase, since the photoreaction proceeds mainly in the acetonitrile phase.

Recovery of Aromatics from Acetonitrile and Effect of Addition of Water. Aromatic hydrocarbons are distributed between the two phases together with the sulfur-containing compounds, as shown in Table 1. In order to recover the sulfur-free aromatics from the acetonitrile phase, a liquid–liquid extraction procedure was employed, using light paraffinic solvent (*n*-hexane) as the stripping solvent. Tetrahydronaphthalene (tetralin, 95 mM) and naphthalene (50 mM), being typical of one- and two-ring aromatics, respectively, were added to a DBT/acetonitrile solution ($[DBT]_{initial}$ = 12 mM) which had been treated by 2 h of photoirradiation, and then the solution was contacted with *n*-hexane. Figure 11 shows the extractability of these compounds as a function of the *n*-hexane/acetonitrile volume ratio. At

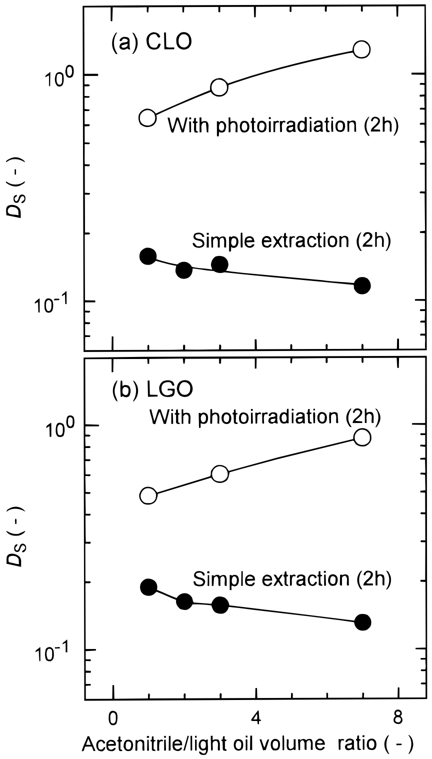

Figure 10. Effect of the photoirradiation on the sulfur distribution ratio, D_S, in (a) commercial light oil (CLO)/acetonitrile and (b) straight-run light gas oil (LGO)/acetonitrile systems. D_S: ratio of the total sulfur content in acetonitrile and in light oils.

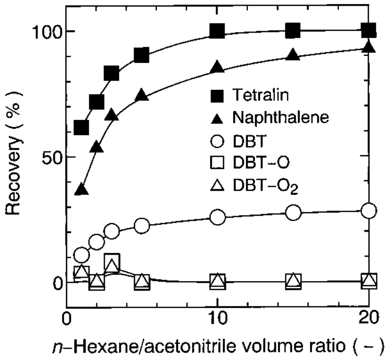

Figure 11. Extractability of aromatic hydrocarbons and photo-oxidized compounds of DBT after 2 h of irradiation from DBT/acetonitrile by n-hexane.

volume ratios of up to 10, sulfur-free aromatics recoveries of over 85% were obtained for naphthalene and those of 100% were obtained for tetralin. Similar results were also obtained for the extraction, when using n-heptane and n-pentane. DBT also tends to be extracted; however, it is possible to suppress the transfer to the paraffinic phase by further irradiative conversion to DBT-O and DBT-O_2. Hexane and acetonitrile can be easily separated from the aromatics and the photodecomposed DBTs by evaporation or distillation and may be reused in the desulfurization process.

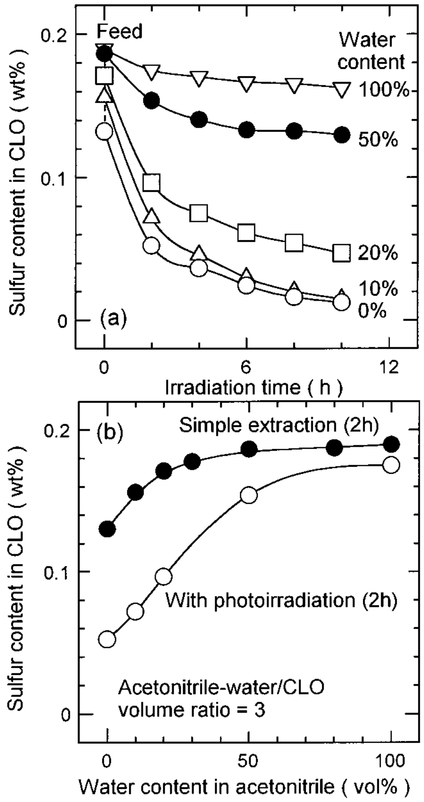

Figure 12. Effect of the addition of water in acetonitrile on (a) the time-course variation of sulfur content in the commercial light oil (CLO) and (b) the sulfur content in the CLO at 2 h in the case with and without photoirradiation.

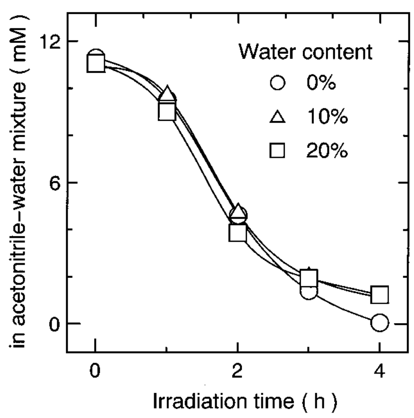

Figure 13. Time-course variation in the DBT concentrations in acetonitrile/water mixed solvents, during photoirradiation.

When contacted, a quantity of acetonitrile is actually distributed into the light oil phase. Some water is usually added to the polar solvents such as DMSO, sulfolane, and tetraethylene glycol to improve the selectivity in the separation and purification of the aromatics (Bailes, 1983). Thus, the effect of the addition of water on the desulfurization process and on the recovery of the aromatics was also investigated. Phase separation was found to be improved, and dissolution of the solvent into the light oil was suppressed by using mixed solvents. This was especially the case with the addition of 10–20 vol % of water. The desulfurization yield of CLO was decreased by increasing water content, as shown in Figure 12. The photoreactivity of DBT in mixed solvents, however, was not influenced by the addition of water within 20 vol %, as shown in Figure 13. The decrease in the desulfurization yield at water contents of 10–20 vol % was attributed to a decrease in the simple distribution of the sulfur compounds into the mixed solvent phase. The desulfurization of light oil by photoirradiation with 10–20 vol % of a water/acetonitrile mixed solvent was, therefore, found to be fairly feasible.

It is important to extract as much of the aromatics as possible into the n-hexane, while leaving as much

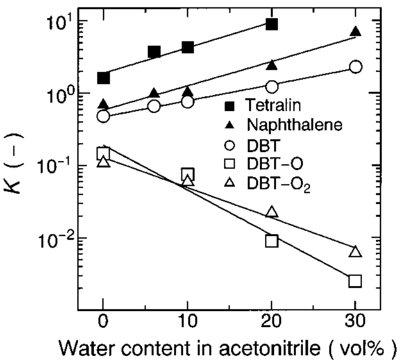

Figure 14. Effect of the addition of water to acetonitrile on the distribution coefficient, *K*, of aromatic hydrocarbons and DBT derivatives.

Table 4. Separation Factor β (=K/K_{DBT-O}) in the Extraction of DBT Derivatives and Aromatic Compounds from Acetonitrile by *n*-Hexane

	water content (vol %)			
	0	10	20	30
$\beta_{Naphthalene}$	4.67	13.7	262	2768
$\beta_{Tetralin}$	11.1	57.5	993	
β_{DBT}	3.29	10.1	135	924

DBT and its derivatives as possible in the acetonitrile/water solution. To study this, a DBT/acetonitrile ($[DBT]_{initial}$ = 15 mM) solution was photoirradiated for 3 h and then water was added to the solution. The solutions were then contacted with an equal volume of *n*-hexane. Figure 14 shows the effect of the water content on the distribution coefficient, *K*, defined as the ratio of the concentration of the aromatic hydrocarbons and DBT derivatives in *n*-hexane to those in the acetonitrile/water mixture. With increasing water content, the values of *K* for the aromatic hydrocarbons are increased, as reported by Natusch and Tomkins (1974), while the values for DBT-O and DBT-O_2 are decreased, probably caused by the increase in the polarity of the acetonitrile phase by the addition of water. Thus, the separation factor, β, which represents $K_{Naphthalene}/K_{DBT-O}$ and $K_{Tetralin}/K_{DBT-O}$, is increased to more than 900 by the addition of water to acetonitrile, as shown in Table 4. Thus, in this way, the quantitative recovery of pure aromatics from the solvent phase is more easily effected. On distilling the resulting mixed solvent following re-extraction, an azeotropic mixture (84% acetonitrile and 16% water, 76 °C) containing no sulfur compounds was obtained. This means that the pure azeotropic mixture can be recovered and reused as the extraction solvent.

Organization of the Process. A basic flow scheme of the overall process involving the extraction and photodecomposition of sulfur-containing compounds, the recovery of aromatics, and then solvent recovery is given in Figure 15. Feed light oil and an azeotropic mixture are introduced to the photoreactor for the desulfurization. Then, the extraction phase (acetonitrile phase) is sent to the aromatics extractor. The aromatics compounds are extracted by the light paraffinic solvent such as *n*-hexane, leaving the photodecomposed sulfur-containing compounds. The solvent was mixed with desulfurized light oil and can easily be recovered by distillation, and therefore, all the sulfur-free aromatics from the feed are mixed with the raffinate light oil phase. By choosing an appropriate mixture ratio of the solvent and desulfurized light oil, the raffinate containing a required amount of aromatics can be obtained at the bottom of the distillation tower. The water is used to wash the raffinate for recovery of dissolved acetonitrile, and the water phase is then mixed with the remaining extraction phase (acetonitrile) which contains sulfur-containing compounds. Pure azeotropic mixtures are recovered by the distillation, and the pure water was recovered by the sequential distillation, leaving the photooxidized and photodecomposed sulfur-containing compounds at the bottom. The water can be recovered and reused for the washing solvent of raffinate. In this overall process, therefore, the extraction phase (acetonitrile/water azeotropic mixture), aromatic recovery solvent (*n*-paraffin), and water can be recirculated.

Conclusion

A novel deep desulfurization process for light oil, employing a combination of photochemical reaction and organic two-phase liquid–liquid extraction has been investigated, with the following results.

(1) The photoconversion of DBTs was found to proceed effectively in acetonitrile. The energy transfer from the excited-state DBT to ground-state aromatic molecules was much reduced in acetonitrile. The DBT was photoconverted first to DBT-O and then to DBT-O_2, DBT sultine, and aromatic anionic sulfur compounds by a sequential photoreaction. These oxygenated compounds are highly polarized and are therefore not distributed into the light oil phase.

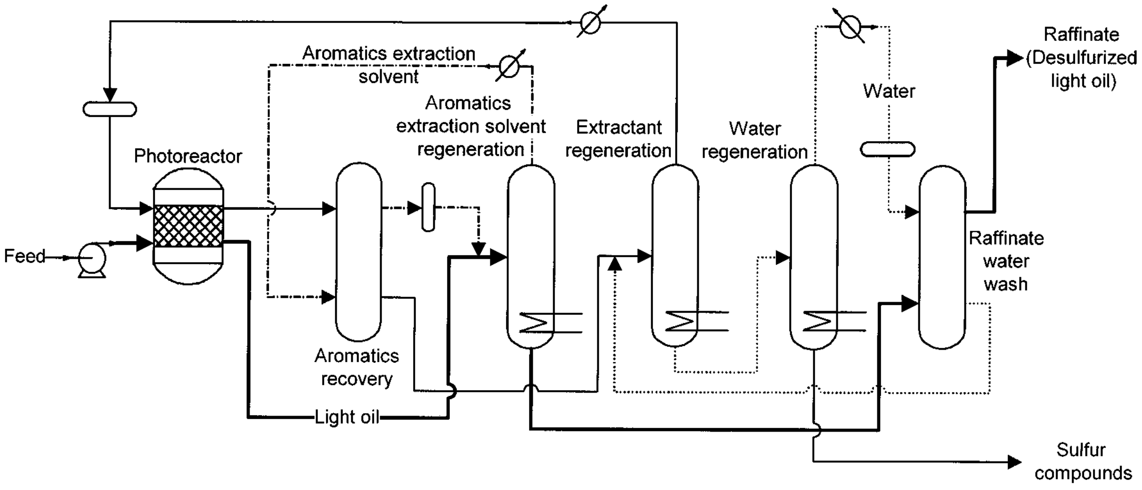

Figure 15. Flow scheme of the deep desulfurization process for light oil.

(2) The desulfurization yield for commercial light oil (CLO) and straight-run light gas oil (LGO) was drastically enhanced, by a combination process of the extraction of the sulfur-containing compounds into acetonitrile following the photochemical reaction. The sulfur contents for CLO were reduced from 0.2 to 0.05 wt % by 2 h of irradiation, and those for LGO were reduced from 1.4 to 0.05 wt % by 10 h of photoirradiation.

(3) The coextracted sulfur-free aromatic hydrocarbons were easily recovered by extraction from the acetonitrile phase using light paraffinic hydrocarbons, leaving highly polarized photodecomposed compounds of DBTs in the acetonitrile. This separation was performed with greater ease by the addition of 10−20% water into the acetonitrile. The overall flow scheme of the desulfurization process for light oil was proposed, in which all the solvents and water can be recirculated.

Acknowledgment

The authors acknowledge members of Cosmo Research Institute for their help with GC−AED analysis. The authors are grateful for the financial support by Grant-in-Aid for Scientific Research (No. 09555237) from the Ministry of Education, Science, Sports and Culture, Japan. I.K. acknowledges also The Sumitomo Foundation for financial support. Y.S. acknowledges financial support from The Morishita Zintan Scholarship Foundation.

Literature Cited

Akasaka, T.; Yabe, A.; Ando, W. Charge-transfer Photooxygenation of Sulfides in a Cryogenic Oxygen Matrix: IR Spectroscopic Observation of Persulfoxides. *J. Am. Chem. Soc.* **1987**, *109*, 8085−8087.

Bailes, P. J. Aromatics−Aliphatics Separation. In *Handbook of Solvent Extraction*; Lo, T. C., Baird, M. H. I., Hanson, C., Eds.; John Wiley & Sons: New York, 1983; Chapter 18.2.

Chatgilialoglu, C.; Gilbert, B. C.; Gill, B.; Sexton, M. D. Electron Spin Resonance Studies of Radicals formed during the Thermolysis and Photolysis of Sulphoxides and Thiolsulphonates. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1141−1150.

Gerdil, R.; Lucken, E. A. C. The Electron Spin Resonance Spectra of the Dibenzothiophene Radical Anion and Its Isologs and the Electronic Structure of Conjugated Sulfur-Containing Heterocycles. *J. Am. Chem. Soc.* **1965**, *87*, 213−217.

Gilman, H.; Esmay, D. L. The Oxidation of Dibenzothiophene and Phenoxathiin with Hydrogen Peroxide. *J. Am. Chem. Soc.* **1952**, *74*, 2021−2024.

Hanson, G.; Kemp, D. S. Convenient Routes to 4,4″-Functionalized *o*-Terphenyls and 2,2′-Functionalized Biphenyls. *J. Org. Chem.* **1981**, *46*, 5441−5443.

Hirai, T.; Ogawa, K.; Komasawa, I. Desulfurization Process for Dibenzothiophenes from Light Oil by Photochemical Reaction and Liquid−Liquid Extraction. *Ind. Eng. Chem. Res.* **1996**, *35*, 586−589.

Hirai, T.; Shiraishi, Y.; Komasawa, I. Desulfurization Process for Light Oil by Photochemical Reaction and Liquid−Liquid Extraction: Removal of Benzothiophenes and Alkyl Sulfides. *J. Chem. Eng. Jpn.* **1997a**, *30*, 171−173.

Hirai, T.; Shiraishi, Y.; Ogawa, K.; Komasawa, I. Effect of Photosensitizer and Hydrogen Peroxide on Desulfurization of Light Oil by Photochemical Reaction and Liquid−Liquid Extraction. *Ind. Eng. Chem. Res.* **1997b**, *36*, 530−533.

Jenks, W. S.; Lee, W.; Shutters, D. Photochemistry of Aromatic sulfoxides. 1. Characterization of the Triplets at Cryogenic Temperatures. *J. Phys. Chem.* **1994a**, *98*, 2282−2289.

Jenks, W. S.; Taylor, L. M.; Guo, Y.; Wan, Z. Photochemistry of Dibenzothiophene-*S*,*S*-dioxide: Reactions of a Highly Constrained Biradical. *Tetrahedron Lett.* **1994b**, *35*, 7155−7158.

Kabe, T.; Ishihara, A.; Tajima, H. Hydrodesulfurization of Sulfur-Containing Polyaromatic Compounds in Light Oil. *Ind. Eng. Chem. Res.* **1992**, *31*, 1577−1580.

Khudayer, A. F. Studies on the Photolytic behavior of Dibenzothiophene in Crude Oil/Water System. *Diss. Abstr. Int., B* **1991**, *51*, 3303.

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

Natusch, D. F. S.; Tomkins, B. A. Isolation of Polycyclic Organic Compounds by the Solvent Extraction with Dimethyl Sulfoxide. *Anal. Chem.* **1978**, *50*, 1429−1434.

Tezuka, T.; Miyazaki, H.; Suzuki, H. On the Photo-Oxidation of Sulfides in the Presence of Oxygen. *Tetrahedron Lett.* **1978**, *22*, 1959−1960.

Vignier, F.; Berthou, F.; Picart, D. Influence of Injection Systems on the Gas Chromatographic Analysis of Oxygenated Dibenzothiophenes. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1983**, *6*, 661−665.

Zannikos, F.; Lois, E.; Stournas, S. Desulfurization of Petroleum Fractions by Oxidation and Solvent Extraction. *Fuel Process. Technol.* **1995**, *42*, 35−45.

Received for review June 2, 1997
Revised manuscript received September 22, 1997
Accepted October 1, 1997[⊗]

IE970388F

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.