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Photocatalytic oxidation of dibenzothiophenes in acetonitrile using TiO$_2$: effect of hydrogen peroxide and ultrasound irradiation

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Abstract

Photocatalytic oxidation of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6DMDBT) in acetonitrile using titanium dioxide (TiO$_2$) was studied. Results obtained here can be used as the reference for evaluating reactions in hydrocarbons, which aims at the development of an oxidative desulfurization process for oils. A 200 W Hg–Xe lamp (>290 nm, 19 mW/cm^2) was used as a light source, and the catalytic performances of four commercially available TiO$_2$ photocatalysts (PC-1, PC-2, PC-3 and P25) were compared.

DBT was more stable than 4,6DMDBT under light and in the presence of photocatalyst in acetonitrile. Of the photocatalysts used, P25 showed the highest rate of photooxidation. However with P25, the decrease in initial concentration of DBT or 4,6DMDBT was less than 40% after 10 h of irradiation. To accelerate the reaction, the effect of addition of hydrogen peroxide (H$_2$O$_2$) and/or ultrasound irradiation on the TiO$_2$-containing system was studied. Although the addition of hydrogen peroxide (3%) and/or ultrasound irradiation more than doubled the rate of photooxidation, this efficiency was obtainable with H$_2$O$_2$ alone. Tentatively identified reaction products from DBT and 4,6DMDBT included the 5-oxide (sulfoxide) and the 5,5-dioxide (sulfone) of each substrate. Oxidation of the methyl group mainly occurred when 4,6DMDBT was reacted using only TiO$_2$. This result led to a finding that the acceleration of oxidation for the methyl group occurs in non-polar hydrocarbons. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photooxidation; Desulfurization; Photocatalyst; TiO$_2$; Dibenzothiophene; 4,6-Dimethyldibenzothiophene

1. Introduction

Catalytic hydrodesulfurization is commonly used to decrease the sulfur content of oil. Desulfurization is generally conducted at high pressure (>50 kg/cm^3) and high temperature (>250 °C) by reacting hydrogen gas with sulfur compounds in the presence of a catalyst. Hydrogen sulfide (H$_2$S) is mainly produced. Among the various sulfur compounds in oil, dibenzothiophenes (DBTs) are the most resistant to hydrogenation and require the use of a modified catalyst and more severe reaction conditions [1].

Sulfur compounds in petroleum products can cause problems. Combustion of heavy oils containing more than 0.1% of sulfur compounds emits sulfur dioxide (SO$_2$), which causes asthma in humans. This is a major problem in industrial cities of the developing countries. Recently, attention has been focused on decreasing the sulfur content in gas oil for diesel engines. Catalyst efficiency in removing NO$_x$ and particulate matter (PM) from diesel exhaust is adversely affected by the presence of sulfur compounds in gas oil,

and it is important to decrease the sulfur content in gas oil below 50 ppm (deep desulfurization). However, deep desulfurization requires the use of a modified catalyst and more severe reaction conditions to enable stable DBTs to react with hydrogen, making deep desulfurization an expensive process.

To save energy and reduce costs, an alternative desulfurization process needs to be developed. For this purpose, some oxidative desulfurization processes which include oxidation of DBTs with oxidants followed by the removal of products have been investigated [2]. As one of the processes, photochemical reaction with sunlight as an energy source is also promising. Although DBT is stable against direct photolysis [3,4], slow photooxidation occurs in natural and simulated marine environments [3–6]. Patel et al. [5] observed formation of compounds with sulfoxide moieties from DBT and its C1-, C2-, and C3-alkyl homologs. Later, Payne and Phillips [4] and Berthou and Vignier [6] reported that DBT sulfoxide and DBT sulfone are formed by photolysis of DBT. Although Mill et al. [3] detected five products by HPLC, attempts to characterize these products by GC–MS were unsuccessful. Andersson and coworkers [7–9] later reported details about the photochemical

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degradation and degradation products from DBTs. According to Berthou and Vignier [6] and Andersson [7], alkylated DBTs are more stable than DBT on the surface of water.

Several research groups have recently demonstrated photooxidative desulfurization of oil. Hirai et al. [10–16] achieved deep desulfurization of gas oils by photooxidizing DBTs. They developed several processes, including photooxidation in solution followed by liquid–liquid extraction of the oxidation products. Meille et al. [17] and Shiraishi et al. [18,19] used photoinduced charge-transfer reactions (oxidation) for desulfurization. Although the desulfurization rate for gas oil with these methods was over 50%, irradiation time was generally long (>5 h). Using a photocatalyst may reduce the time for the treatment. However for photocatalytic oxidation, only one report by Abdel-Wahab and Gaber [20] was present for DBT and no report was found for 4,6-dimethyldibenzothiophene (4,6DMDBT). Abdel-Wahab and Gaber [20] used anatase-type TiO_2 produced by Aldrich and obtained information about the conversion rate and products in acetonitrile.

Here, we report results on photooxidation of DBT and 4,6DMDBT in acetonitrile using another commercially available titanium dioxide (TiO_2) including well-known P25. The effect of addition of hydrogen peroxide (H_2O_2) and/or ultrasound irradiation on the TiO_2-containing system is also reported. We chose acetonitrile as the solvent for the reaction since this solvent is relatively stable and gives results usable for comparison. Furthermore, addition of H_2O_2 and ultrasound irradiation was examined in order to increase the rate of oxidation reaction. The results obtained here can be used as the reference for evaluating reactions in hydrocarbons, which aims at the development of the photooxidative desulfurization process.

2. Experimental section

2.1. Chemicals

DBT and 4,6DMDBT were purchased from Aldrich (Wisconsin, USA) and ACROS (Belgium), respectively. HPLC-grade acetonitrile (Aldrich) was used as a solvent for the reaction. DBT 5,5-dioxide (sulfone) (Aldrich) was used for identification of oxidation products.

Four kinds of TiO_2 powder were used as photocatalysts: P25 (Aerosil, Japan) and PC-1, PC-2 and PC-3 (Ishihara Sangyo, Japan). The authors altered the names of the latter three products. The characteristics of the TiO_2 photocatalysts are given in Table 1. Except for PC-3 (rutile-type), the main crystalline type of TiO_2 is anatase. For PC-1 and PC-2, high efficiencies for photodecomposition of volatile gases such as acetaldehyde and ammonia have been reported [21]. H_2O_2 solution (30%, Wako Pure Chemicals Industries) was used as an oxidation agent.

Table 1
Characteristics of titanium dioxide (TiO_2) used in this study

Photocatalyst	Particle size (nm)	Specific surface area (m^2/g)	Main crystalline type
P25	21	50	Anatase
PC-1	7	300	Anatase
PC-2	7	250	Anatase
PC-3	–	30	Rutile

2.2. Apparatus

Sample solutions were photoirradiated in a glass reactor consisting of two parts: a vessel with a volume of 200 ml and a quartz cap with an inlet tube for introducing air and an outlet tube for releasing air and gaseous products. A magnetic stirrer (Pasolina TR-100) under the reactor was used to stir the solution except when ultrasound irradiation was applied to accelerate photooxidation. For ultrasound irradiation, a sonifier (Bransonic 12, 45 kHz, 50 W) with a constant volume of water was used instead of the magnetic stirrer. Keeping a constant water depth was necessary to produce the same strength of ultrasound for each experiment. Artificial air (O_2: 21%, N_2: 78%) was introduced from a gas cylinder at a flow rate of 10 ml/min through a needle valve to dissolve O_2 in the acetonitrile solution. A 200 W Hg–Xe lamp (Sanei Denki Seisaku-sho, 19 mW/cm^2) was used as the light source for photoirradiation. Light from this lamp was directed into the glass reactor through a glass fiber cable and the quartz cap. A filter was placed before the quartz cap to remove shorter wavelengths of light (<290 nm). During photoirradiation, the glass reactor was wrapped with aluminum foil to shield against other laboratory light sources.

2.3. Photoirradiation and analysis

Photooxidation experiments were carried out as follows. An acetonitrile solution of DBT or 4,6DMDBT (100 ml, 5×10^{-4} M) was placed in a glass vessel and 0.2 g of TiO_2 was added to the solution. The solution was photoirradiated for 0–10 h with continuous bubbling of air and magnetic stirring (or ultrasound irradiation). After 1, 2, 4, 6, 8 and 10 h of photoirradiation, samples (2 ml) were collected from the glass vessel and analyzed to determine substrate concentration and reaction products. Prior to analysis, samples were centrifuged to remove fine TiO_2 particles. An HPLC apparatus equipped with a UV–Vis photodiode array detector (Shimadzu SPD-M10A) and a fluorescence detector (JASCO FP-929A) was mainly used for analysis. Substrate and reaction products were separated on an Inertsil ODS-2 column (GL Sciences, 4.6 mm i.d. ×250 mm) using acetonitrile/water (76/24) eluent. Capillary gas chromatographs with a sulfur-selective detector (Sievers Model 355) and an EI-MS detector (Hewlett-Packard HP5971) were also used to identify reaction products. An HP-5MS column (0.32 mm i.d. ×30 m, 0.25 μm film thickness, Hewlett-Packard) and

HP-50 column (0.25 mm i.d. ×30 m, 0.25 μm film thickness, Hewlett-Packard) were used. The temperature of the injection port of the gas chromatograph was kept relatively low (200 °C) since DBT oxides decompose at 250 °C [5]. Absorption spectra of the products observed with the SPD-M10A HPLC detector were also used for identification. Thermal analysis (TGA and DTA) and infrared spectral analysis of the TiO$_2$ powders were respectively carried out with a Shimadzu DTG-50 thermal analyzer and a Nicolet Magna 560 FT-IR spectrometer equipped with a diamond ATR accessory (DuraScope, SensIR Technologies).

The rate constants for the apparent consumption of DBT (or 4,6DMDBT) were obtained from the relation:

$$-\ln\left(\frac{C_t}{C_0}\right) = k_p t \qquad (1)$$

where C_0 and C_t are the concentrations of substrate at time zero and time t (s), and k_p the first-order rate constant (s^{-1}). Half-lives ($t_{1/2}$ (s)) were calculated using Eq. (2), which was derived from Eq. (1) by replacing C_t with $C_0/2$

$$t_{1/2} = \frac{0.693}{k_p} \qquad (2)$$

Values obtained in seconds were converted to hours.

3. Results and discussion

3.1. Effect of the presence of photocatalyst (TiO$_2$) on photooxidation of DBT and 4,6DMDBT in acetonitrile

The effect of the presence of TiO$_2$ on the photooxidation of DBT and 4,6DMDBT in acetonitrile was assessed

from plots of $-\ln(C_t/C_0)$ vs. t obtained with and without photocatalyst (TiO$_2$: P25) (Fig. 1). In the absence of photocatalyst (white square and a solid line), DBT (Fig. 1, left panel) did not react at all even after 10 h of photoirradiation. We confirmed that the decrease in DBT concentration was quite small up to 50 h. However, when TiO$_2$ was present in the solution (black triangle and a solid line), photooxidation of DBT occurred more rapidly. After 10 h of irradiation, $-\ln(C_t/C_0)$ was 0.356, which means C_t/C_0 was about 0.7. Thus, after 10 h of irradiation, the decrease in DBT concentration was about 30%. 4,6DMDBT (Fig. 1, right panel) was somewhat more reactive than DBT. The concentration decreased slightly in the absence of photocatalyst (white square and a solid line). A value of 0.94 was obtained for C_t/C_0 after 10 h of photoirradiation, which indicates that the concentration decreased by 6%. When TiO$_2$ was present (black triangle and a solid line), 4,6DMDBT reacted more rapidly, as in the DBT case. After 10 h of photoirradiation, $-\ln(C_t/C_0)$ was 0.462, which means that the 4,6DMDBT concentration decreased by about 37%. The rate constants (k_p) and half-lives ($t_{1/2}$) for reactions of DBT and 4,6DMDBT with and without photocatalyst (TiO$_2$: P25) are listed in Table 2. With photocatalysis, 4,6DMDBT had slightly larger k_p and slightly shorter $t_{1/2}$ values than did DBT. In case of DBTs, the oxidation of sulfur occurs by the electrophilic addition reaction of oxygen atoms [2]. Therefore the higher is the electron density of a sulfur atom in a sulfur-containing compound, the higher is the reactivity of oxidation. Higher reactivity for 4,6DMDBT may be attributed to higher electron density of a sulfur atom donated by two methyl groups.

Also listed in Table 2 are the rate constants and half-lives obtained for photooxidation of 4,6DMDBT with three other
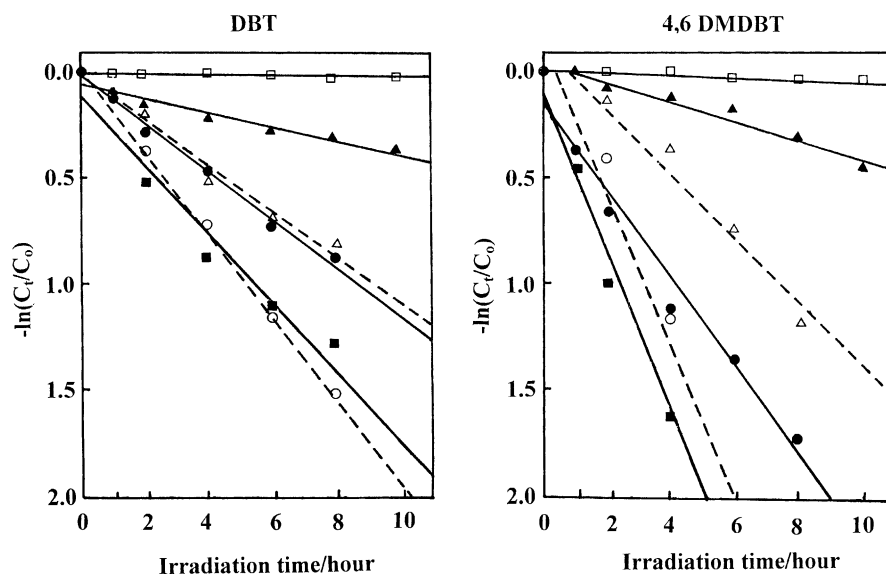

Fig. 1. Photooxidation of DBT and 4,6DMDBT in acetonitrile under various conditions: (–□–) without photocatalyst; (–▲–) with photocatalyst (TiO$_2$: P25); (–△–) with photocatalyst and ultrasound irradiation; (–●–) with H$_2$O$_2$ and photocatalyst; (–○–) with H$_2$O$_2$, photocatalyst and ultrasound irradiation; (–■–) with H$_2$O$_2$ alone.

Table 2
Rate constants and half-lives for photooxidation of DBT and 4,6DMDBT in acetonitrile

Substrate	Photocatalyst	Rate constant (s^{-1})	Half-life (h)
DBT	None	$-^a$	$-^a$
DBT	P25	9.74×10^{-6}	19.8
4,6DMDBT	None	1.83×10^{-6}	105
4,6DMDBT	P25	1.21×10^{-5}	15.9
4,6DMDBT	PC-1	7.31×10^{-7}	263
4,6DMDBT	PC-1 (calcinated)	2.67×10^{-6}	72.1
4,6DMDBT	PC-2	1.38×10^{-6}	139
4,6DMDBT	PC-3	3.18×10^{-6}	60.5

^{a} These values could not be calculated since the concentration of substrate did not change.

TiO_2 photocatalysts (PC-1, PC-2 and PC-3). In these cases, the concentration of 4,6DMDBT decreased very slowly compared with the P25 case and the rate constants were on the order of 10^{-6} or 10^{-7}. The activity of anatase-type TiO_2 (PC-1 and PC-2) was lower than the activity of rutile-type TiO_2 (PC-3), contrary to prediction. Thermal analysis and ATR infrared spectral measurements revealed that PC-1 and PC-2 contained more adsorbed water than P25 and PC-3. In thermal analysis, PC-1 and PC-2 showed a strong endothermic peak in the DTA curve in the range 70–80 °C and a decrease in TG % above 80 °C. The difference in water content is more clearly indicated in the reflective infrared absorption spectra measured using ATR for the four kinds of TiO_2 (Fig. 2). The absorbance in the 3100–3600 cm^{-1} range, where the O–H stretch of water molecules appears is weak for P25 and PC-3, whereas a broad band with a

stronger absorption appears below 3400 cm^{-1} for PC-1 and PC-2. This difference in infrared absorption may be related to the method used to synthesize the TiO_2 (wet or dry method). Although detailed information is not available, PC-1 and PC-2 are synthesized in solution and P25 and PC-3 are synthesized at high temperature. We examined the effect of heat treatment (350 °C, 15 h) on the activity of PC-1 and found that such treatment resulted in the increase in the rate of photooxidation (see results for PC-1 (calcinated) in Table 2). This means that the activity of TiO_2 is partly controlled by water content. Active sites on TiO_2 surface may be covered with water molecules or water–acetonitrile clusters [22,23]. As apparent from Table 2, reaction rate after heat treatment is still low compared with that of P25. We therefore suppose that other factors (e.g. the surface area and the purity of the TiO_2 crystallite) affect the activity. More detailed studies are needed to explain the difference in photooxidation activity for TiO_2.

As described above with the most effective photocatalyst (P25), the decrease in concentration of DBT and 4,6DMDBT after 10 h of photoirradiation was only about 30 and 37%, respectively. Practical applications of photocatalytic oxidation require improvement in reaction efficiency. Thus, we studied the effect of addition of H_2O_2 and ultrasound irradiation on the P25-containing system.

3.2. Effect of addition of hydrogen peroxide (H_2O_2) to the TiO_2-containing system

We studied the effect of adding H_2O_2 to the TiO_2 (P25)-containing system for the photooxidation of DBT and
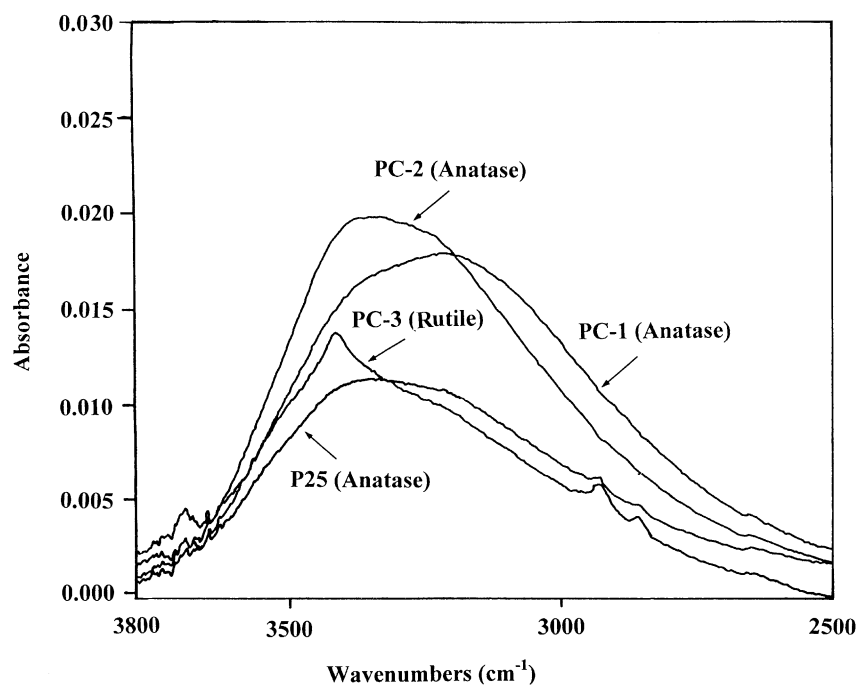

Fig. 2. Reflective infrared absorption spectra of TiO_2 used in this study.

4,6DMDBT. The $-\ln(C_t/C_0)$ vs. t relationships obtained with photocatalyst (TiO_2: P25) and H_2O_2 are also shown in Fig. 1 with black circles and solid lines. Since the rate of reaction decreased when more than 3% of H_2O_2 was added, the concentration of H_2O_2 was kept at 3% (10 vol.% of a commercial 30% H_2O_2 solution in a sample solution). We think that the decrease in the rate of reaction is caused by an increase in the water content in the acetonitrile solution. We previously confirmed that the solubility of oxygen in acetonitrile solution decreases with increasing water content [24]. A decrease in oxygen content results in a low rate of reaction. The relations, in Fig. 1, for P25–H_2O_2 systems show that the rates of reaction for DBT (left panel) and 4,6DMDBT (right panel) increase with the addition of H_2O_2. When H_2O_2 was added, the value of $-\ln(C_t/C_0)$ became larger than 0.5 (40% reacted) after 6 h of photoirradiation for DBT and after 2 h of photoirradiation for 4,6DMDBT. However, as can be seen from Fig. 1, the rates of reactions obtained when both P25 and H_2O_2 were used are slower than when H_2O_2 was used alone (black square and a solid line). Depression of the reaction may occur when the two reaction accelerators are combined. Nakano [25] obtained a similar result in case of the study on decolorization of water. He reported that depression of the activity for TiO_2 occurred when H_2O_2 was added to anatase-type TiO_2. Poisoning of anatase TiO_2 surface by H_2O_2 [26] may cause such an adverse effect. The rate constants and half-lives obtained for the P25–H_2O_2 systems are listed in Table 3.

When H_2O_2 is added, OH radicals may not be efficiently formed from H_2O_2 in the solution since UV absorption by H_2O_2 at wavelengths above 290 nm is very weak. The high efficiency with H_2O_2 alone (Fig. 1) may be due to direct oxidation. We confirmed that DBT in 3% H_2O_2–acetonitrile solution gives 0.54 for $-\ln(C_t/C_0)$ (42% reacted) under stirring for 8 h without light. Therefore, the increase in the rate of reaction for the P25–H_2O_2 system may be attributed to direct oxidation by H_2O_2. In this case, the efficiency for direct oxidation by H_2O_2 is depressed by the presence of TiO_2.

3.3. Effect of ultrasound irradiation on the TiO_2-containing system

We also investigated the effect of ultrasound irradiation on the photooxidation of DBT and 4,6DMDBT for the TiO_2-containing system. In Fig. 1, results for the system containing only TiO_2 (P25) are plotted with white triangles and a dotted line and those for the system containing both TiO_2 (P25) and H_2O_2 are plotted with white circles and a dotted line. For both systems, the rates of photooxidation of DBT and 4,6DMDBT increased with ultrasound irradiation. Rate constants and half-lives are listed in Table 3. For both DBT and 4,6DMDBT with ultrasound irradiation, the rate constant for the P25 system increased by a factor of 3 and that for the P25–H_2O_2 system increased by a factor of 1.7. Using 4,6DMDBT as the substrate, we confirmed that no reaction occurred with ultrasound irradiation alone, i.e. in the absence of TiO_2 or light. In other words, the oxidation reaction is controlled not by ultrasound irradiation, but rather by a photocatalytic effect. Ultrasound does however accelerate the photocatalytic reaction.

For the effect of ultrasound irradiation, we expected the prevention of agglomeration for TiO_2 fine particles and the increase in the surface area usable for photooxidation. However, Kado et al. [27] recently reported, for their work on photocatalytic oxidation of aliphatic alcohols, that the particle size of the TiO_2 powder decreases for the initial period (<1 min) and then increases (the surface area decreases) by ultrasound irradiation. Therefore the cause of acceleration was not attributed to an increase in the surface area. Kado et al. [27,28] suggested that ultrasound activate the surface of TiO_2 and this phenomenon and enhancement of mass transfer accelerate the reactivity. We think that oxidation of DBTs were similarly accelerated by these effects. In addition, Kado et al. [27] reported that reaction condition such as ultrasound power, stirring speed, amount of TiO_2, concentration of substrate and pretreatment of TiO_2 powder affect the oxidation reaction.

As described above, photooxidation in the TiO_2 and TiO_2–H_2O_2 systems can be accelerated with ultrasound irradiation. However, the efficiencies achieved are still low or similar compared with that obtained with H_2O_2 alone (see Fig. 1 and Table 3).

3.4. Products formed by photocatalytic oxidation of DBT and 4,6DMDBT

Fig. 3 shows structures of tentatively identified reaction products of DBT and 4,6DMDBT. For DBT, the main products identified by GC–MS and UV absorption spectroscopy were DBT 5-oxide (DBT sulfoxide) and DBT 5,5-dioxide (DBT sulfone) regardless of whether the oxidizing agent was TiO_2 or H_2O_2. The formation of these products is consistent with the results obtained by Abdel-Wahab and Gaber [20]. The mass spectrum of DBT 5-oxide contains fragment ion peaks at m/z 200, 184, 171, 152 and 139, and that of
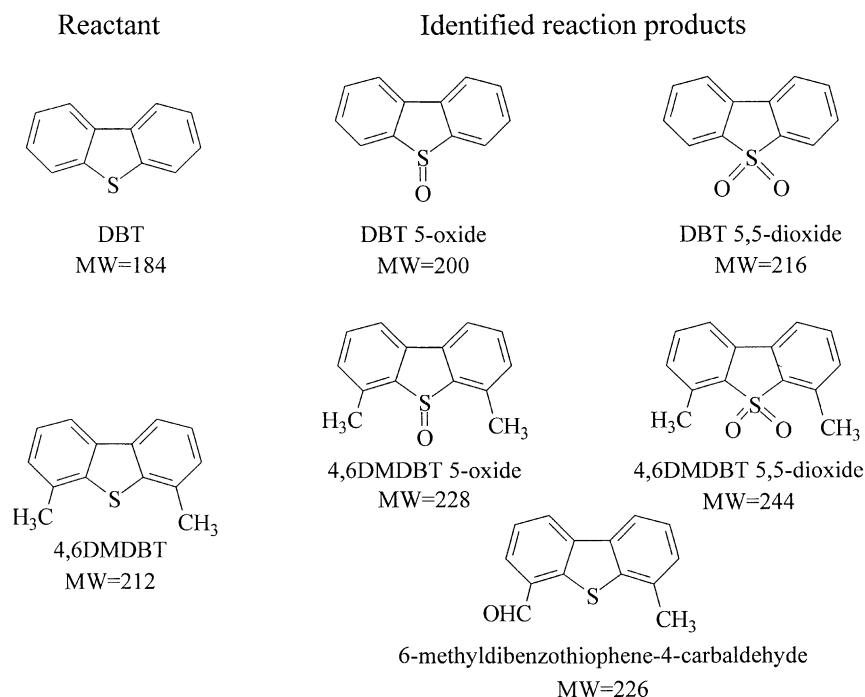
Table 3

Rate constants and half-lives for photooxidation of DBT and 4,6DMDBT in acetonitrile with the addition of hydrogen peroxide and/or ultrasound irradiation

Substrate	Additive[a]	Rate constant (s^{-1})	Half-life (h)
DBT	P25–H_2O_2	3.1×10^{-5}	5.6
DBT	H_2O_2	4.4×10^{-5}	4.3
DBT	P25–UI	2.9×10^{-5}	6.7
	P25–H_2O_2–UI	5.3×10^{-5}	3.6
4,6DMDBT	P25–H_2O_2	5.7×10^{-5}	3.3
4,6DMDBT	H_2O_2	1.0×10^{-4}	2.2
4,6DMDBT	P25–UI	4.1×10^{-5}	4.1
	P25–H_2O_2–UI	9.7×10^{-5}	2.0

[a] Abbreviations: P25, TiO_2: P25; H_2O_2, hydrogen peroxide; UI, ultrasound irradiation.

Reactant   Identified reaction products

Fig. 3. Reaction products of DBT and 4,6DMDBT.

DBT 5,5-dioxide contains those at m/z 216, 187, 168, 160, 139 and 115. When the system contained H_2O_2 alone, we also detected smaller amounts of two co-products that eluted from the HPLC column more slowly than the two main products. In addition, the results showed that ultrasound irradiation accelerated the oxidation of DBT 5-oxide to DBT 5,5-dioxide in the P25–H_2O_2 system. Specifically, a larger amount of DBT 5,5-dioxide was formed under ultrasound irradiation than when magnetic stirring was employed. This is the effect of activation of TiO_2 surface and enhancement of mass transfer by ultrasound irradiation [27].

In contrast, 4,6DMDBT yielded a different main product depending on the oxidation agent (TiO_2 or H_2O_2). When the system contained only P25, a compound that shows fragment ion peaks at m/z 226, 197, 165 and 152 was mainly formed. This compound was assumed to be 6-methyldibenzothiophene-4-carbaldehyde, which is formed by oxidation of the methyl group. In addition, minor amounts of other products were detected by HPLC and GC–MS. Compounds with parent mass fragment (M^+) at 228, 244 and 279 were formed when magnetic stirring was employed, while compounds with M^+ at 228, 230 and 244 were detected in the case of ultrasound irradiation. Larger amounts of M^+ 228 and M^+ 224 were formed under ultrasound irradiation. The molecules with M^+ 228 and M^+ 244 are probably 4,6DMDBT 5-oxide and 4,6DMDBT 5,5-dioxide, respectively. The UV absorption spectra for these compounds resembled those of DBT 5-oxide and DBT 5,5-dioxide and were red-shifted about 6 nm compared with spectra of oxygenated DBTs.

The structures of the molecules with M^+ 230 and M^+ 279 are not clear at present. We recently found that oxidation of the methyl group, which occurs as a main reaction in the presence of only P25, is accelerated by more than 10 times in non-polar hydrocarbons [29]. The rate constant of $1.0 \times 10^{-4}\,\text{s}^{-1}$ was obtained in a 2:1:2 mixture of *n*-heptane, 2,2,4-trimethylpentane (isooctane) and methylcyclohexane. Details will be published later.

When H_2O_2 was added to the solution of 4,6DMDBT, no M^+ 226 product was formed. The M^+ 228 product was mainly formed in the absence of TiO_2. Adding TiO_2 to the H_2O_2 system increased the amount of M^+ 244 product obtained. For the TiO_2–H_2O_2 system, more M^+ 244 product was obtained under ultrasound irradiation than when magnetic stirring was employed. Thus ultrasound irradiation increases the rate of photooxidation.

4. Conclusion

We studied the photocatalytic oxidations of DBT and 4,6DMDBT in acetonitrile using TiO_2. We found that DBT is more stable than 4,6DMDBT and that the rate of photooxidation differs depending on the kind of TiO_2. Although P25 showed the highest photooxidation rate, the conversion of DBTs (less than 40% after 10 h of photoirradiation) is inadequate for application (e.g. desulfurization of oils). Adding hydrogen peroxide (3%) to the TiO_2 (P25)-containing system or irradiating the system with ultrasound accelerated the photooxidation. However, these methods were not much

superior to the photooxidation using H_2O_2 alone in the solution. Products from DBT and 4,6DMDBT were tentatively identified. It seems that oxidation of the methyl group mainly occurred when only TiO_2 was used and that addition of oxygen to the sulfur atom in the ring occurred when H_2O_2 was used.

In this paper, we did not describe how oil components affect the photooxidation of DBT and 4,6DMDBT. Hirai et al. [10] previously reported that photosensitized oxidation is depressed in the presence of naphthalene. In contrast, we recently found that non-polar hydrocarbons accelerate the oxidation of methyl group-substituted DBTs [29]. Further studies on avoiding negative effects and increasing the efficiency of the photocatalytic oxidation are in progress in our laboratory and will be reported in the future.

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