PHOTODEGRADATION OF SURFACTANTS
II: DEGRADATION OF SODIUM DODECYLBENZENE SULPHONATE CATALYSED BY TITANIUM DIOXIDE PARTICLES

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Summary

The photocatalytic degradation of an anionic sodium dodecylbenzene sulphonate (DBS) with "naked" TiO_2 powder suspensions has been investigated for its potential use as an antipollutant system. The DBS surfactant (50 ppm) is decomposed efficiently within 1 h under exposure to sunlight. The aromatic group in DBS is easily decomposed, whilst the long aliphatic chain slowly gives rise to partial oxidation. The O_2 consumption, CO_2 evolution, SO_3^{2-} formation, surface tension, repeated catalytic activity and pH dependence have also been examined.

1. Introduction

Many of the surfactants widely used in various applications can cause severe problems for the natural aquatic environment [1]. Their biodegradation and bioelimination through bacteria is slow. Several days or even weeks are required for the complete biodecomposition of surfactants [2]. Photoinduced catalytic decomposition with semiconductors will provide an important route to the environmental degradation of many organic pollutants and toxic substances.

Recent studies have focused on (a) the photodegradation of halogenated aromatics such as polychlorinated biphenyl [3], chlorobenzene [4] and chlorophenols [5] using semiconductor-based catalysts, (b) the photooxidation of halogenated aliphatics [6] and carboxylic acid [7] and (c)

the photocatalytic oxidation and its mechanism of aliphatic and aromatic compounds with naked TiO_2 and $Pt-TiO_2$ catalysts [8, 9].

Except for a short note from our laboratories [10], no reports have appeared on the photodegradation of surfactants employing aqueous semiconductor dispersions.

This paper reports the efficient degradation of sodium dodecylbenzene sulphonate (DBS) by a heterogeneous photoassisted process using TiO_2 (anatase) suspensions.

2. Experimental details

DBS $(CH_3(CH_2)_{11}C_6H_4SO_3Na)$, sodium dodecyl-1-sulphate (SDS; $CH_3(CH_2)_{11}OSO_3Na$) and sodium benzene sulphonate (BS; $C_6H_5SO_3Na$; purity, 97%) were used as supplied by Fluka and were at least reagent grade. Water was distilled twice in a quartz still. The TiO_2 employed was Degussa P-25 (mainly anatase with surface area 55 $m^2\ g^{-1}$). The TiO_2 particles doped with RuO_2 (0.5, 1, 1.5, 3 and 6 wt.%) and platinum (0.73 wt.%) were kindly supplied by Nukem G.m.b.H., F.R.G.

Aqueous dispersions (25 ml) of 2 g l^{-1} TiO_2 were contained in a Pyrex glass reaction vessel (37 ml; closed with a septum) and were stirred magnetically. During photolysis, the reaction temperature was about 37 °C.

Two procedures were employed to examine the effect of O_2 on the overall photocatalytic processes.

(1) *Open system.* No prior argon purging of the slurry was used to remove O_2 or CO_2 from the distilled water. The semiconductor slurry was in contact with air by means of two needles placed through the septum.

(2) *Closed system.* The TiO_2 suspension, contained in the reaction vessel closed with a septum, was purged with argon for about 30 min, followed by addition of O_2 gas; the system was kept closed to air at all times.

Irradiation was carried out either with the $\lambda > 330$ nm output of a 450 W xenon lamp equipped with a 15 cm water jacket (to remove IR radiation) or with the light output of a suntest lamp (Hanau). The global irradiance of the suntest lamp in the wavelength region 340 - 830 nm was about 100 mW cm^{-2}, the spectral distribution of the light intensity reflecting AM1 solar radiation. The power output of the xenon lamp was about 80 mW cm^{-2}. Solar experiments were also performed on a sunny day (60 mW cm^{-2}) and a cloudy day (10 mW cm^{-2}) of November 1984, in Lausanne. The TiO_2-surfactant solution was stirred under solar exposure.

Changes in the concentration of DBS present in the supernatant solution obtained by centrifuging the slurry for 10 min with an Eppendorf Centrifuge (Model 5414; 12 000 rev min^{-1}), were observed by monitoring the spectral changes in the 224 nm absorption band (Hitachi-Perkin-Elmer 340 UV-visible spectrophotometer). The oxygen consumption was determined with a GOW-MAC gas chromatograph using a Carbosieve 5-A column (35 °C) and argon as the carrier gas. Changes in pH were monitored with an

Orion digital pH meter. Potential intermediates in the photodegradation were identified by proton nuclear magnetic resonance (NMR) and IR spectroscopy. $SO_3{}^{2-}$ ions were detected by ion exchange chromatography on a Wescan 261 Ion Analyzer equipped with a Wescan 213A conductivity detector and a Wescan standard column 269.001; a solution of potassium hydrogen phthalate (0.8 g l^{-1}, pH 3.9) was used as an eluent. In all cases, the contribution of $SO_3{}^{2-}$ from a blank run (2 g l^{-1} suspension of TiO_2–surfactant) was taken into account.

The surface tension of the solutions was measured with a Gouy–Chapman balance meter (Krüss Surface Tensiometer K8451) at ambient temperature; the TiO_2 particles had been removed previously by centrifuging for at least 7 min.

CO_2 formed in the reaction was detected by formation of barium carbonate in a $Ba(OH)_2$ solution; the reaction gases, after a long irradiation time, were swept out of the reaction vessel with a stream of nitrogen and were bubbled through consecutive solutions of $Ba(OH)_2$. These solutions were collected, and the excess $Ba(OH)_2$ was titrated with a standard 0.1 N HCl solution.

3. Results and discussion

The photochemical or thermal degradation of organic pollutants can be classified into three processes: (I) a primary degradation necessary to alter the character or the properties of the substances; (II) a secondary degradation process that is environmentally acceptable; (III) a final degradation process that leads ultimately and quantitatively to the mineralization of the organic substrate to CO_2 and H_2O. In the present instance, a primary degradative process for the surfactants might consist in the cleavage of a certain portion of the amphiphilic surfactant molecules as witnessed by a change in the surface activity.

For the complete decomposition of DBS, O_2 is an important ingredient, as indicated below, in as much as no degradation occurs under anaerobic conditions.

$$CH_3(CH_2)_{11}C_6H_4SO_3Na + 25O_2 \longrightarrow 18CO_2 + 14H_2O + NaHSO_3$$
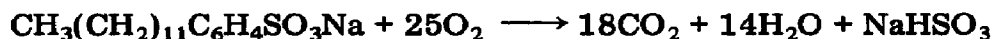
Even if complete mineralization does not occur, suppression of the surface activity of the surfactant might still occur via desulphonation or via decomposition of the aromatic component of DBS. A variety of intermediates will be formed during the total mineralization to CO_2 and H_2O.

The photodecomposition of DBS as a function of irradiation time is illustrated in Fig. 1. Illumination of an aqueous solution of DBS (50 ppm in 25 ml) in the presence of suspended TiO_2 causes rapid decomposition (at least 90%) of the phenyl moiety in DBS in less than 30 min under simulated solar radiation by a suntest lamp (118 mV cm^{-2}). Irradiation with the 450 W xenon lamp (96 mW cm^{-2}; wavelengths longer than 330 nm) leads
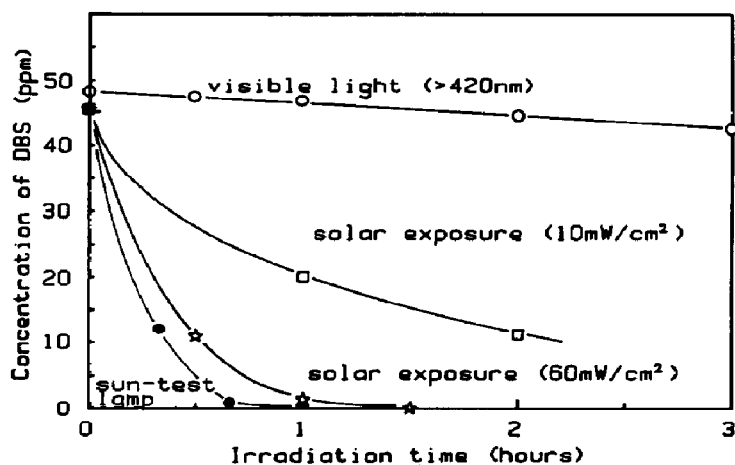
Fig. 1. Photodegradation of DBS in aqueous TiO_2 dispersions: ○, visible light irradiation ($\lambda > 420$ nm); □, solar exposure on a cloudy day (10 mW cm^{-2}); ☆, solar exposure on a sunny day (60 mW cm^{-2}); ●, suntest (450 W, $\lambda > 320$ nm). (A 25 ml aliquot of DBS (50 ppm) with 50 mg TiO_2 is placed in a 37 ml reaction bottle under aerated conditions. The amount of DBS as calculated from the peak difference of the absorption and its baseline at 222 nm is plotted as a function of irradiation time.)

to the same results. In the dark and even after 7 h of light exposure in the absence of TiO_2, the DBS surfactant shows no signs of decomposition. Some slight degradation occurs upon light exposure for 4 days. To try a practical application under a solar exposure, reaction vessels containing the surfactant solution of TiO_2 suspension were placed outdoors on a cloudy day (10 mW cm^{-2}) and a sunny day (60 mW cm^{-2}). The decomposition rate on a sunny day was faster than that on a cloudy day, but the slower degradation arises from the lower irradiance available under practical experimental conditions. In fact, the photodecomposition requires high energy photons. Visible light irradiation ($\lambda > 420$ nm) of a TiO_2–DBS aqueous suspension permits the recovery of unchanged DBS even after 3 h irradiation.

No traces of DBS were observed after 2 h simulated solar exposure. When a more concentrated DBS solution (500 ppm in 25 ml) was used, 24 h were required for the decomposition of the phenyl substituent in DBS. As a comparison, the degradation of BS under identical conditions was also examined. Total decomposition of the benzene ring occurred in less than 83 min irradiation. It is also noteworthy that DBS decomposes faster than BS under identical conditions. This is because DBS becomes adsorbed on the surface of the semiconductor particles where oxidation occurs.

Figure 2 depicts the oxygen consumption against irradiation time for an aqueous solution of DBS in the presence of TiO_2. The rate of oxygen consumption reaches a plateau after about 2.5 h. By contrast, the surfactant-free slurry exhibits little consumption of oxygen (about 200 μl after 6 h, against 1200 μl after 5 h). The apparent oxygen consumption in the TiO_2–DBS slurry in the dark is probably the result of slow adsorption of oxygen onto TiO_2 because of the interfering surfactant. The consumption of oxygen in
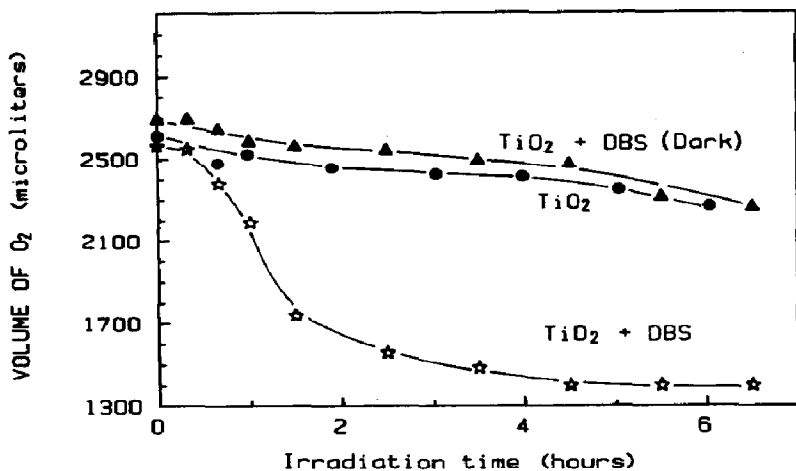
Fig. 2. Oxygen consumption during the photolysis of TiO_2 dispersions in the absence and presence of DBS (50 ppm) under xenon-lamp irradiation ($\lambda > 330$ nm) and under the dark reaction for aqueous DBS solution containing TiO_2 particles. The solutions were purged with argon prior to O_2 injection.
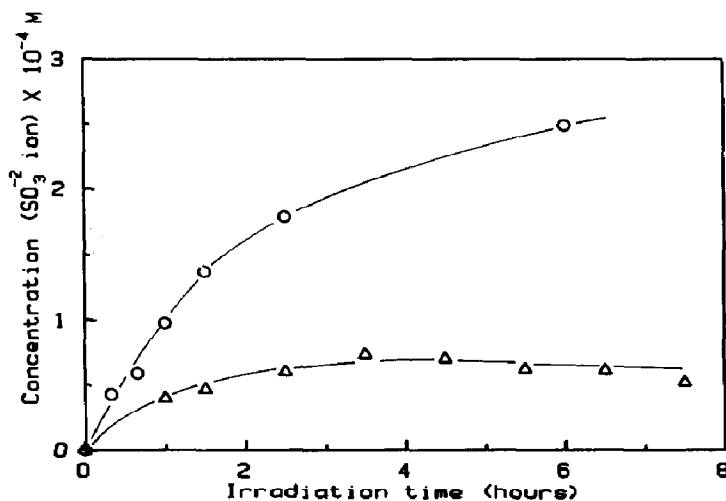

Fig. 3. SO_3^{2-} ion formation under xenon-lamp irradiation ($\lambda > 330$ nm) for DBS (50 mg l^{-1}) and BS (50 mg l^{-1}) in the presence of TiO_2 (50 mg in 25 ml solution): $\triangle$, DBS (50 ppm); $\circ$, BS (50 ppm).

the TiO_2–DBS irradiated slurry is accompanied by the formation of SO_3^{2-} ions in the aqueous solution. Here, also, the concentration of SO_3^{2-} reaches a plateau after about 2.5 h irradiation (cf. Fig. 3).

Further evidence for alterations in the nature of the DBS surfactant is illustrated in Fig. 4, where changes in surface tension as a function of irradiation time for three different concentrations of DBS are shown. The 1000 ppm DBS solution (2.8 mM) shows an increase in surface tension to 65 dyn cm^{-1} after 6 h illumination. The 500 ppm solution, where the concentration of DBS is close to its critical micelle concentration (1.59 mM at
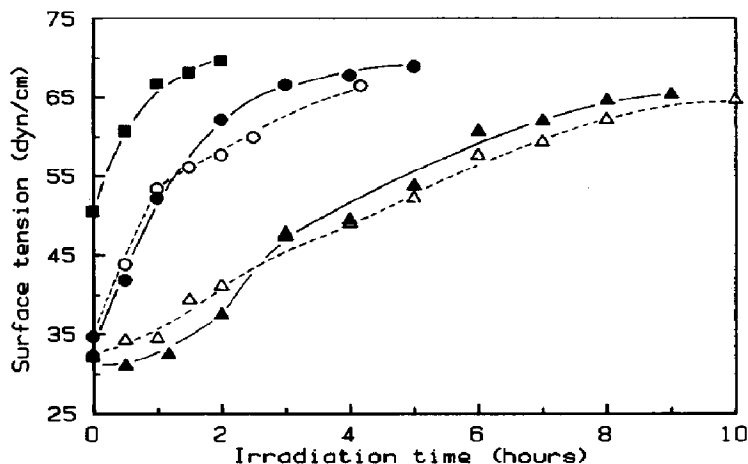
Fig. 4. Surface tension of DBS or SDS (25 ml) *vs.* irradiation time in aqueous TiO_2 (50 mg) dispersions (illumination using a xenon lamp; $\lambda > 330$ nm): ■, DBS (50 ppm, 0.14 mM); ●, DBS (500 ppm, 1.4 mM); ▲, DBS (1000 ppm, 2.8 mM); ○, SDS (500 ppm, 1.74 mM); △, SDS (1000 ppm, 3.47 mM). (Literature-cited critical micelle concentrations: DBS, 1.59 mM (553 ppm) [11]; SDS, 8 mM (2306 ppm) [12].)
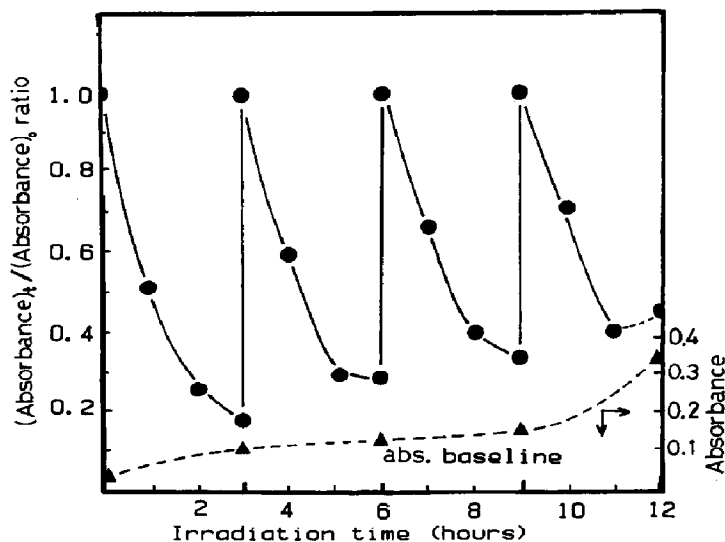

Fig. 5. Repetitive use of TiO_2 for the decomposition of the DBS surfactant. OD_t is the optical density after irradiation for a fixed time t and OD_0 is the initial optical density before the further addition of TiO_2. ▲ represents the initial optical density and that after each 3 h of irradiation.

30 °C) reaches the plateau after about 2.5 h, a fact which is consistent with the data noted earlier. By contrast, when the DBS concentration is below the critical micelle concentration (50 ppm), irradiation leads to a rapid increase in surface tension to 65 dyn cm^{-1} after only 0.5 h.

For comparison, the photodegradation of SDS, which does not have an aromatic ring, was also explored. The decomposition of SDS is slower
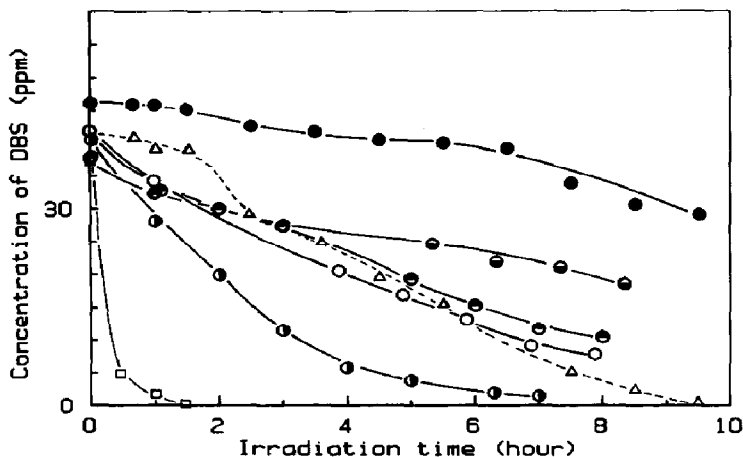
Fig. 6. Catalytic activity of TiO_2–Pt and TiO_2–RuO_2 for the degradation of DBS: □, TiO_2 only; △, TiO_2–0.73wt.%Pt; ○, TiO_2–0.5wt.%RuO_2; ◑, TiO_2–1wt.%RuO_2; ◒, TiO_2–1.5wt.%RuO_2; ◓, TiO_2–3wt.%RuO_2; ●, TiO_2–6wt.%RuO_2. (The amount of photo-degraded DBS was determined from the intensity of the peak at 222 nm. A 25 ml solution of DBS (50 ppm) in the presence of each catalyst (50 mg) was irradiated with a xenon lamp.)

than that of DBS. If a surfactant can be cleaved partially at a certain position, *e.g.* C—SO_3Na, the resulting compounds from the surfactant decomposition would have hydrophobic properties and exhibit no surface activity.

In Fig. 5, the turnover activity of TiO_2 under the experimental conditions described earlier is examined. A 50 ppm DBS–TiO_2 slurry was irradiated for 3 h to complete decomposition of the surfactant. Following this, a further 1.3 mg DBS was added to the slurry to bring the concentration of DBS to 50 ppm. Irradiation was continued and the process repeated three or four times.

Since noble metal catalysts deposited on the surface of semiconductor particles often lead to a more efficient reductive system (*e.g.* H_2 evolution), semiconductor dispersions of naked TiO_2 doped with 0.73 wt.% Pt, and TiO_2 doped with 0.5, 1, 1.5, 3 and 6 wt.% RuO_2, were investigated and compared.

The results of this study are summarized in Fig. 6. While we expected to see an acceleration in the rate of decomposition in the presence of noble catalysts, the plots of Fig. 6 indicate otherwise. The presence of platinum slows down the decomposition rate considerably. The RuO_2-loaded catalyst similarly exhibits a poor degradation in comparison with the naked TiO_2 catalyst.

The 1 wt.% RuO_2 catalyst is more effective than the 6 wt.% RuO_2 catalyst, which is essentially inactive in the photodegradation of DBS. This may be because it is all covered with RuO_2 and the aqueous suspension is too greyish-black to allow transmission of light. The naked TiO_2 is still relatively efficient.

Decomposition of the surfactants leads to formation of H^+ ions. The changes in pH as a function of irradiation time are shown in Fig. 7. The
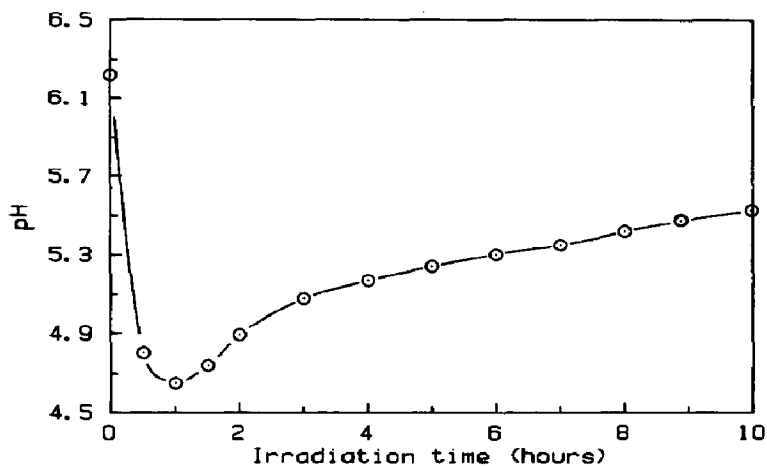
Fig. 7. pH *vs.* irradiation time (irradiation with xenon lamp, $\lambda > 330$ nm) for 25 ml DBS (50 ppm) solution in the presence of TiO$_2$ (50 mg) at ambient temperature.
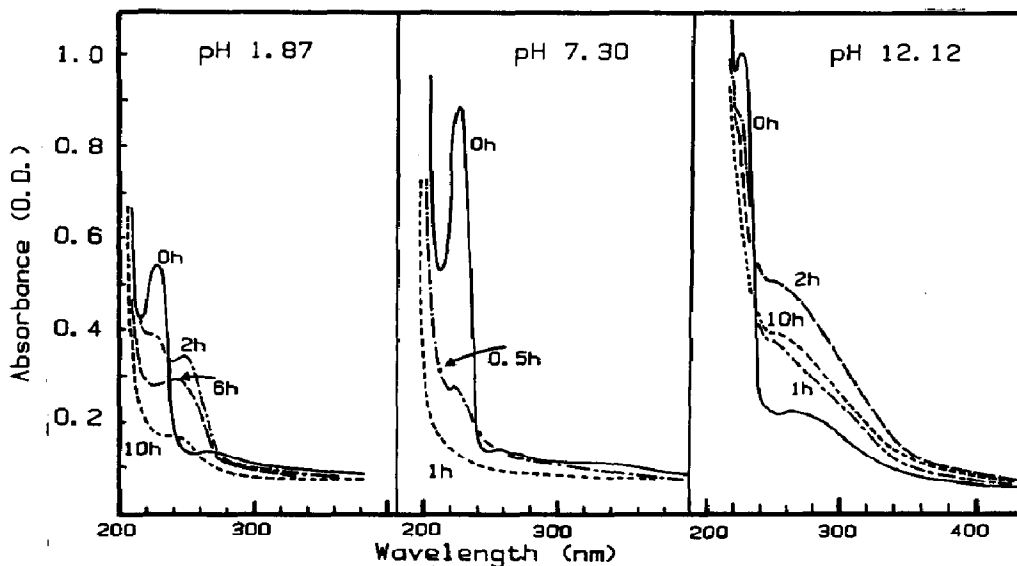

Fig. 8. Spectral change of photodegradation for 50 ppm DBS at pH 1.87, pH 7.30 and pH 12.12. (A 25 ml solution of DBS (50 ppm) in the presence of TiO$_2$ (50 mg) was irradiated under aerated conditions with a xenon lamp (100 mW cm^{-2}; $\lambda > 330$ nm).)

initial DBS–TiO$_2$ slurry has a pH of 6.3. Irradiation rapidly leads to decomposition as noted earlier with a concomitant increase in the H$^+$ concentration (decrease in pH) after about 1 h. Following this, the pH increases gradually to reach a plateau of pH about 5.2. TiO$_2$ is an amphoteric substance with an isoelectric point of 5.6; the surface potential is negative in the neutral pH region, leading to adsorption of H$^+$ via hydrogen bonding. The excess of TiO$_2$ over DBS yields a buffered solution.

Figure 8 shows UV spectral changes of DBS *versus* irradiation time in acidic (pH 1.87), neutral (pH 7.3) and alkaline (pH 12.12) solutions. In

TABLE 1

CO_2 evolution for the decomposition of DBS, SDS and BS

Surfactant	Concentration (ppm)	Irradiation time (h)	Equivalent CO_2 per initial equivalent
DBS	200	3	2.5
DBS	50	15	4.2
SDS	200	3	0.8
SDS	50	15	1.1
BS	50	3	1.9 ± 0.3
BS	50	15	5.8 ± 0.2
4-Chlorophenol	64	3	5.9 ± 0.1

Conditions: 20 ml solution; TiO_2, 2.0 g l^{-1}; suntest lamp ($\lambda > 315$ nm).

neutral solution, the $\pi-\pi^*$ absorption band (222 nm) of the phenyl group in DBS rapidly decreases in intensity and after 1 h irradiation there is no further signal. Therefore photodecomposition is excellent in the neutral pH solution. In acidic solution, the $n-\pi^*$ absorption band (261 nm) appears and the $\pi-\pi^*$ absorption (222 nm) disappears after 2 - 6 h irradiation. Even after 10 h irradiation, the $n-\pi^*$ band is still discernible. By contrast, in alkaline solution the disappearance of the band and the appearance of the $n-\pi^*$ band are remarkable. Consequently, DBS decomposition is not facilitated in alkaline solutions.

The extent of decomposition of the aromatic moiety was also monitored by the determination of CO_2 released from the photodegradation of DBS, SDS and BS, using $Ba(OH)_2$. The results are summarized in Table 1.

While the aromatic group in DBS is easily decomposed to yield CO_2, the aliphatic chain in DBS undergoes only slight decomposition to CO_2 even after long irradiation periods. In the case of the 50 ppm solution of DBS, 4.2 equivalents of CO_2, which corresponds to 23.3% (ultimate mineralization yield), are formed per equivalent of DBS after 15 h illumination. By comparison, only 1.1 equivalents of CO_2 per equivalent of SDS (mineralization yield, 9.2%) are formed. Clearly, 15 h of light exposure does not lead to complete mineralization to CO_2 and H_2O. BS (mineralization yield, about 97% for 15 h) and 4-chlorophenol (mineralization yield, 98% for 3 h), which have no alkyl chains, are photodegraded easily and completely to CO_2 and H_2O (and/or HCl, H_2SO_4) by a suntest lamp irradiation.

Photo-oxidation of alkanes [13], alkenes [14], aromatics [15], alcohols [16], carboxylic acids [17] and other substrates by semiconductor particle systems has been widely examined. Photochemical oxidation mechanisms have been proposed from the identification of the intermediates. By analogy, we consider the mechanisms in the degradation of the DBS surfactant.

Following the cleavage of the aromatic group from the alkyl chain to yield a cation radical at the α position, subsequent oxidative steps presum-

ably yield, in turn, peroxides, alcohols, aldehydes, carboxylic acids and percarboxylic acids. Finally CO_2 is evolved via a cation radical with a shorter alkyl chain. Further degradation may occur by oxidation of this cation radical (ω position), which will eventually lead to total decomposition. The overall photodegradation is initiated by irradiation of the DBS–TiO_2 aqueous suspension. The primary photoprocess involves the formation of electron–hole pairs, which generates highly oxidizing sites at the surface of the semiconductor particles.

The proposed mechanism postulates trapping of electron holes by surface hydroxyl groups to give OH· radicals and trapping of electrons by O_2 to form adsorbed O_2^- species [18].

Single-electron transfer from an adsorbed organic molecule to the excited semiconductor leads to the formation of a radical cation whose subsequent dark reactions control the net observed reactivity. Transient formation of intermediates through single-electron transfer events may be detected by laser flash photolysis of DBS–colloidal TiO_2 sols.

We have attempted to identify some of the possible intermediates by IR and NMR spectroscopy following 2 days irradiation of a slurry of DBS and TiO_2. The IR spectra clearly indicate the formation of carboxylic fatty acids, which show a strong —COOH absorption band at about 1718 nm in addition to bands due to the aliphatic chain (C—H) at 2840 - 2980 nm.

The NMR spectra of a DBS solution (in D_2O) show weak non-resolvable four-proton resonances of the phenyl group at about 7 ppm (against trimethylsilane), a terminal methyl proton resonance, two rather intense signals assigned to the methyl proton resonance and two rather intense signals assigned to the methylene protons of the alkyl chain. Irradiating the DBS–TiO_2–D_2O solution for 4 days causes the disappearance of the phenyl resonances, but the methylene signals are still evident. This indicates that the aromatic moiety has decomposed but that the aliphatic chain is indeed slow to decompose. Moreover, the irradiated solution no longer shows surface activity such as foaming power. The DBS surfactant has undergone an environmentally acceptable degradation.

4. Conclusions

Illumination of semiconductor particles with light provides an important route to the photodegradation of surfactants such as DBS. While the alkyl chain of DBS is slow to yield total mineralization to CO_2 and H_2O, as observed for other substrates, the surface tension results demonstrate that even such surfactants as SDS and BS undergo environmentally acceptable primary or secondary degradation. The present findings are significant for waste treatment processes in which surfactants are important constituents.

Acknowledgments

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