PAPER

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Dynamics and mechanistic features in the photocatalyzed oxidation of disulfonated anionic surfactants on the surface of UV-irradiated titania nanoparticles†

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The photocatalyzed transformation of the anionic 4-dodecyl-1,1′-oxybisbenzenedisulfonate (DOBS) surfactant and its derivatives was carried out in aqueous TiO_2 dispersions under UV and aerated illumination conditions to examine the dynamics and the mechanistic features of the degradative processes. Spectroscopic and other methodologies were used to probe the break-up of the aromatic ring, the mineralization of the surfactant(s) to carbon dioxide, decay of total organic carbon (TOC) remaining in solution, formation of sulfate ions, and identification of oxidation intermediates (*e.g.*, acetic acid, formic acid and acetaldehyde) by NMR spectroscopy. Adsorption of DOBS, in particular, and the other anionic surfactant derivatives in general, on the TiO_2 particle surface was inferred from the calculated point charges. Frontier electron densities of all atoms ascertained the positions of $^{\bullet}OH$ radical attack on the DOBS molecular skeleton. A model for the initial adsorption behavior of DOBS through electrostatic forces between the anionic surfactant(s) and the cationic TiO_2 particle surface is proposed, aided by evidence from ζ-potential measurements. It is deduced that $^{\bullet}OH$ radicals attack preferentially the carbon atoms bonded to the sulfonate groups on the DOBS aromatic rings, followed by further attack on the remaining carbon atoms of the aromatic rings first and then more slowly on the carbon atoms of the hydrophobic alkyl chain.

Introduction

The anionic surfactant sodium 4-dodecyl-1,1′-oxybisbenzenedisulfonate (DOBS) is a widely employed industrial product. In particular, it is used as an emulsifying agent in polymerizations and as a dispersion agent in paints. Because of its strongly acidic and alkaline properties it is a detergent of choice for the cleansing of glassware, aircrafts, trains, and metals. DOBS has the peculiar characteristic of low-foaming power among several other anionic surfactants. It retains its surface activities in both strongly acidic and alkaline pH regions. DOBS surfactant is highly toxic (oral LD_{50} in rats: 700 mg kg^{-1}), as are other anionic surfactants.[1,2] It is also a severe irritant to human skin and eyes. Biodegradation of this surfactant with bacteria is slow and inefficient. Accordingly, an alternative technology is worth considering to safely dispose of such toxic substances as anionic surfactants in aquatic ecosystems.[2] One of many Advanced Oxidation Technologies available for remediation of wastewaters is the TiO_2-mediated photocatalytic methodology. To our knowledge, the photocatalytic degradation of tetralin by this methodology was first reported by Kato and Mashio.[3] A similar study on the photocatalytic degradation of sodium dodecylbenzenesulfonate (DBS) was carried out some two decades later.[4] In recent studies we reported kinetic and mechanistic studies on the photodegradation of a variety of surfactants of differing chemical structures and nature, most notably surfactants possessing anionic,[5,6] cationic,[7] nonionic,[8] and amphoteric[9,10] properties.

A surfactant such as DOBS is an attractive model substrate to examine because it can potentially manifest interesting mechanistic features of the photocatalytic decomposition process, owing to the presence of both hydrophilic and hydrophobic groups. Employing an amphiphilic surfactant to examine the photodegradation process presents some definite advantages because both static factors (*e.g.*, adsorption behavior on the TiO_2 particle surface) and photoinduced dynamic processes can be examined during the photodegradation reaction.

This study examined the photodegradation of the 1,1′-oxybisbenzene structure in the DOBS surfactant. In particular, the degradation dynamics of the two phenyl moieties are compared to those prevailing in the decomposition of the benzene ring in the DBS surfactant. UV/visible spectroscopy, surface tension measurements, total organic carbon assays, ion-chromatographic determination of sulfate ions and other intermediates, and ^1H-NMR spectroscopic methods were brought to bear to unravel the mechanistic details of the process. Frontier electron densities of all atoms in the various surfactant structures were calculated to aid in delineating the possible position(s) of attack of photogenerated $^{\bullet}OH$ radicals on the sulfonate surfactants. In addition, computed point charges were used to assess the mode(s) by which surfactants are adsorbed onto the TiO_2 particle surface, since photodegradation dynamics depend closely on the adsorption behavior.[11]

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† Electronic supplementary information (ESI) available: calculated frontier electron densities and point charges of selected atoms in the DOBS derivatives and in the DBS system taken for comparison. See http://www.rsc.org/suppdata/nj/b4/b402583k/

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Experimental

Materials

Titanium dioxide was Degussa P-25 TiO_2 (surface area, 53 m^2 g^{-1} by BET; particle size, 20–30 nm by TEM observations; crystalline forms, 83% anatase and 17% rutile by XRD analysis). The commercial products consisted of the mixed ingredients Pelex SS-H and Pelex SS-L, and were supplied by Kao Corp., Japan. The long-chain surfactants were synthesized by alkylation of 1,1′-oxybisbenzene with dodecanol in the presence of concentrated H_2SO_4, followed by neutralization with an aqueous NaOH solution. The isomeric products in DBOS were analyzed by reverse-phase chromatography using a Silica ODS column (Crestpack); the eluent was acetonitrile containing $NaClO_4$ (0.1 M) and H_2O (50 : 50 v/v). The predominant ingredient was the disodium salt $C_{12}H_{25}$–$C_6H_3(SO_3^-Na^+)$–O–$C_6H_4SO_3^-Na^+$ with trace quantities of the bisdodecyl homologs; it was hard to determine the concentration of these homologs.

DOBS surfactants consist of two derivatives, one bearing a single dodecyl chain and the other two dodecyl chains, in which the two sulfonate, SO_3^-, groups lie at different positions in the bisbenzene moieties (see structures in Fig. 1).

The DOBS isomers containing only one dodecyl chain are sodium 4-dodecyl-1,1′-oxydiphenyl-2,4′-disulfonate (**A**) and sodium 4-dodecyl-1,1′-oxydiphenyl-3,4′-disulfonate (**B**). In comparison, three DOBS isomers are theoretically possible with two dodecyl chains at the 4,4′positions. These are the sodium 4,4′-bisdodecyl-1,1′-oxydiphenyl-3,2′-disulfonate (**C**), the sodium 4,4′-bisdodecyl-1,1′-oxydiphenyl-3,3′-disulfonate (**D**), and the sodium 4,4′-bisdodecyl-1,1′-oxydiphenyl-2,2′-disulfonate (**E**) derivatives.

The alkylation of 1,1′-oxybisbenzene with dodecanol carried out in concentrated H_2SO_4 led to a variety of isomers. Technical difficulties prevented purification of the disulfonated anionic surfactants, although separation of the isomers was tried by reverse-phase chromatography though to no avail. The UV spectral patterns of DOBS exhibit three maximal absorption bands at 206, 238 and 278 nm. The disappearance of the aromatic group in the 1,1-oxybisbenzene moiety was quantitatively analyzed using the intensity of the 238 nm band. Wako Pure Chem. Ind. special grade anionic dodecylbenzenesulfonate surfactant (DBS) was used as a reference for comparison; it was used without further purification.

Procedures

An aqueous TiO_2 dispersion was prepared by adding TiO_2 (100 mg) particles to a 50 mL aqueous DOBS solution at various concentrations in a 100 mL Pyrex vessel. Prior to irradiation, the dispersions were sonicated in the dark for *ca.* 10 min to ensure achievement of adsorption/desorption equilibrium and purged with oxygen gas. Irradiation of the dispersions was carried out with a 75 W Hg lamp emitting an irradiance of *ca.* 2.0 mW cm^{-2} in the wavelength range 310 to 400 nm (maximal emission at $\lambda = 360$ nm). At given irradiation time intervals, a small sample (4 ml) of the solution was removed, centrifuged and then filtered through a Millipore filter (pore size 0.22 μm) to remove the TiO_2 particles. The DOBS concentration in the filtrate was determined from its UV spectra using a JASCO V-570 spectrophotometer. The surface tension was measured using a Kyowa Interface Sci. CBVP-Z automatic surface tensiometer. The extent of mineralization of the substrates to CO_2 was obtained with a Shimadzu GC-8A gas chromatograph equipped with a TCD detector and a Porapack Q column; helium was the carrier gas. Total organic carbon was measured with a Shimadzu TOC-5000A TOC analyzer. The amount of SO_4^{2-} ions produced in the photodegraded solution was determined on a JASCO Ion chromatograph equipped with an I-524 anionic column and a CD-5 conductivity detector. Proton NMR spectra of D_2O/surfactant solutions were recorded on a JEOL JNM-AL300 spectrometer (300 MHz) using the 3-(trimethylsilyl) propionic-2,2,3,3-d_4 acid sodium salt as the external standard reference enclosed in a capillary tube. The ζ-potential of the titania particles under photocatalytic conditions was measured with a ZEECOM zeta potential analyzer. We measured the ζ potentials for the illuminated solutions containing TiO_2 particles after sampling with a micro cylinder.

Molecular orbital calculations of frontier electron densities and point charges

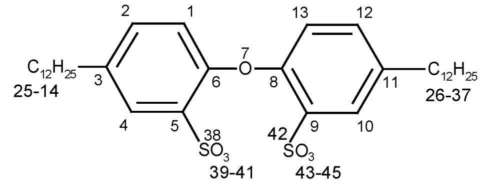
Molecular orbital calculations were carried out at the single determinant (Hartree–Fock) level with the optimal conforma-

(A) Sodium 4-dodecyl-1,1'-oxy-bisbenzene-2,4'-disulfonte

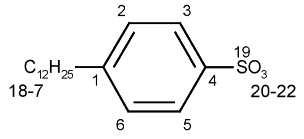
(B) Sodium 4-dodecyl-1,1'-oxy-bisbenzene-3,4'-disulfonte

(C) Sodium 4,4'-bisdodecyl-1,1'-oxy-bisbenzene-3,2'-disulfonate

(D) Sodium 4,4'-bisdodecyl-1,1'-oxy-bisbenzene-3,3'-disulfonate



(E) Sodium 4,4'-bisdodecyl-1,1'-oxy-bisbenzene-2,2'-disulfonate



(F) Sodium dodecylbenzenesulfonate

Fig. 1 Structures of the DOBS and DBS surfactants examined. The numbers on the atoms in these structures are for identifying the atoms for the molecular orbital calculations (see text) and do not correspond to the official IUPAC numbering scheme.

tion of minimum energy obtained at the AMI level. MOPAC version 6 in the CAChe package was used as implemented on a Power Macintosh computer. Molecular orbital calculations provided an understanding of the initial processes of $^{\bullet}$OH radical attack and adsorption of the surfactant on the TiO_2 catalyst surface.

Results and discussion

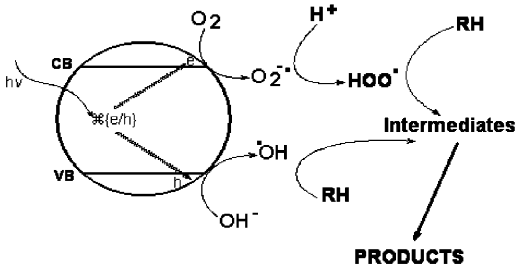
Frontier electron densities and point charges

The three oxygen atoms (O_{31}, O_{32}, O_{33}) of the sulfonate groups in the terminal phenyl ring of the **A** and **B** DOBS homologs have a somewhat greater point charge than the corresponding oxygen atoms of the sulfonate groups located on the other phenyl ring (O_{27}, O_{28}, O_{29}). On the basis of these point charge estimates (see the ESI) we infer that the anionic SO_3^- group in the DBS (**F**) surfactant, which bears the most negative point charges, is electrostatically in contact with the positively charged TiO_2 surface in the aqueous dispersion. Accordingly, the terminal SO_3^- groups bonded to the carbon at position C_{11} in the **A** and **B** isomers are expected to adsorb on the TiO_2 surface more than might be the case of the SO_3^- groups attached, respectively, to the C_5 or C_4 carbon in these isomers. (Note that the numbering of the atoms in Fig. 1 identifies the atom in the MO calculations of Table 1; numbers do not reflect the IUPAC approved numbering scheme of the surfactant structures).

The position of attack of $^{\bullet}$OH radicals on a target atom of an organic substrate is closely related to the frontier electron densities of that atom, since $^{\bullet}$OH radicals are strong electrophiles. That is, the $^{\bullet}$OH radicals will preferentially attack at the electron-rich atoms. For the **A** substrate, the electron density of the carbon atoms decreased in the order: C_5 (4.5059) $\sim$ C_{11} (4.4929) > C_1 (4.2303) > C_3 (4.1881) > C_9 (4.159) $\sim$ C_{13} (4.1572). Accordingly, the C_5 and C_{11} carbon atoms, which are contiguous to the SO_3^- groups, are the likely target of $^{\bullet}$OH radicals. Desulfonation takes place fairly rapidly during the initial period of the photoreaction as evidenced by formation of SO_4^{2-} ions. For the three bisdodecyl derivatives **C**, **D** and **E**, the carbon atoms bonded to the SO_3^- groups with the highest frontier electron densities will be the targets of the $^{\bullet}$OH radicals. The relevant frontier electron densities of the carbon atoms of the **C**, **D** and **E** homologs decrease in the following order: C_9 (4.4833) $\sim$ C_4 (4.4715) > C_{13} (4.1926) > C_{11} (4.1653) $\sim$ C_2 (4.1526) for the **C** homolog, C_4 (4.4590) $\sim$ C_{10} (4.4569) > C_{13} (4.1401) $\sim$ C_2 (4.1385) $\sim$ C_{12} (4.1360) $\sim$ C_1 (4.1349) for the **D** homolog, and C_5 (4.4959) $\sim$ C_9 (4.4913) > C_1 (4.2124) $\sim$ C_{13} (4.2104) > C_3 (4.1711) $\sim$ C_{11} (4.1672) for the **E** homolog. The manner in which the sulfonate groups are bonded in these derivatives (see structures in Fig. 1) makes them adsorb to the TiO_2 surface through both sulfonate groups (see also below). In comparison, the calculated point charges of DBS (**F**) atoms indicate that this surfactant should also be adsorbed on the cationic TiO_2 surface through the anionic SO_3^- group. Consequently, $^{\bullet}$OH radical attack would occur at the C_4 position of DBS first, followed by the C_2 and C_6 carbon atoms.

Proposed model for adsorption and degradation

As shown in Scheme 1, when UV light illuminates a TiO_2 catalyst particle, charge separation ultimately occurs to generate holes in the valence band and electrons in the conduction band. After diffusion of these charge carriers to and trapping at the surface, the carriers are then poised to take part in surface redox reactions. Electrons react with pre-adsorbed O_2 molecules to generate superoxide radical anions, $O_2^{-\bullet}$, whereas the holes react with surface OH^- ions and/or surface chemisorbed water to produce the highly reactive $^{\bullet}$OH radicals. Photooxidation of a chemisorbed water molecule also yields H^+ ions that remain chemisorbed at the surface, making the surface positively charged as evidenced by ζ-potential measurements (see below and ref. 7). Strongly oxidizing $^{\bullet}$OH radicals (and $HOO^{\bullet}$ radicals) typically photooxidize organic substrates, leading to their degradation and ultimate mineralization to CO_2 and water.



Scheme 1

The proposed model for adsorption of DOBS surfactants on the TiO_2 surface and the mode of attack by $^{\bullet}$OH radicals are illustrated in Fig. 2. Two adsorption modes are suggested for the surfactant structure on the particle surface: (i) a perpendicular mode and (ii) a horizontal mode, with respect to the orientation of the long alkyl chain in DOBS, on the basis of electrostatic interactions between the anionic SO_3^- group(s) and the cationic TiO_2 surface. For the **A** and **B** surfactants, and for the DBS surfactant as well, end-on adsorption appears the more likely mode. By contrast, the positions of the sulfonate groups in the **C**, **D** and **F** derivatives are such that a near-horizontal mode is the more likely possibility. Undoubtedly, such adsorption modes will enhance reaction between the surface-bound $^{\bullet}$OH radicals and the target carbon atoms on the phenyl rings.[11]

Zeta potentials and pH changes

Formation of protons accompanies the photogeneration of $^{\bullet}$OH radicals through oxidation of water by the valence band holes. The pH of the aqueous DOBS/TiO_2 dispersion was initially pH 5.8, rapidly shifting to lower pHs (more acidic medium) within 15 min of irradiation, followed by a further, albeit gradual, decrease of pH with further irradiation to attain a final pH *ca.* 3.8 (Fig. 3).

ζ-potential measurements demonstrate that the surface charge of titania particles is more positive with increasing irradiation time. Adsorption of DOBS through the anionic SO_3^- groups on the positive TiO_2 surface is thus facilitated in the more acidic media.

UV/vis spectroscopy, surface tension, and mineralization assays

The temporal break-up (cleavage) of the aromatic groups in the DOBS structure (0.1 mM solution) increased with increasing irradiation time (Fig. 4). Differences between the TiO_2-free stock solution (0.1 mM) and the TiO_2-dispersed solution before UV illumination show that approximately 20% of the surfactant (the c.m.c. of DOBS is 0.1 mM, from surface tension –concentration measurements) did adsorb on the TiO_2 surface under dark equilibrium conditions. In comparison, the initial extent of adsorption of DBS on the TiO_2 surface was *ca.* 40% (0.48 mM; the c.m.c. of DBS is 1.2 mM at 22 °C[12]). It must be noted that DBS adsorbed on TiO_2 is in adsorption equilibrium with the DBS in the bulk solution, some of which appears to desorb on illumination, as is also the case for DOBS (0.1 mM).

UV illumination of the TiO_2/surfactant dispersion causes cleavage of the aromatic ring as noted by loss of aromatic absorption bands at wavelengths below 300 nm (inset of Fig. 4). Degradation intermediates that form at the interface can diffuse back into the bulk solution.

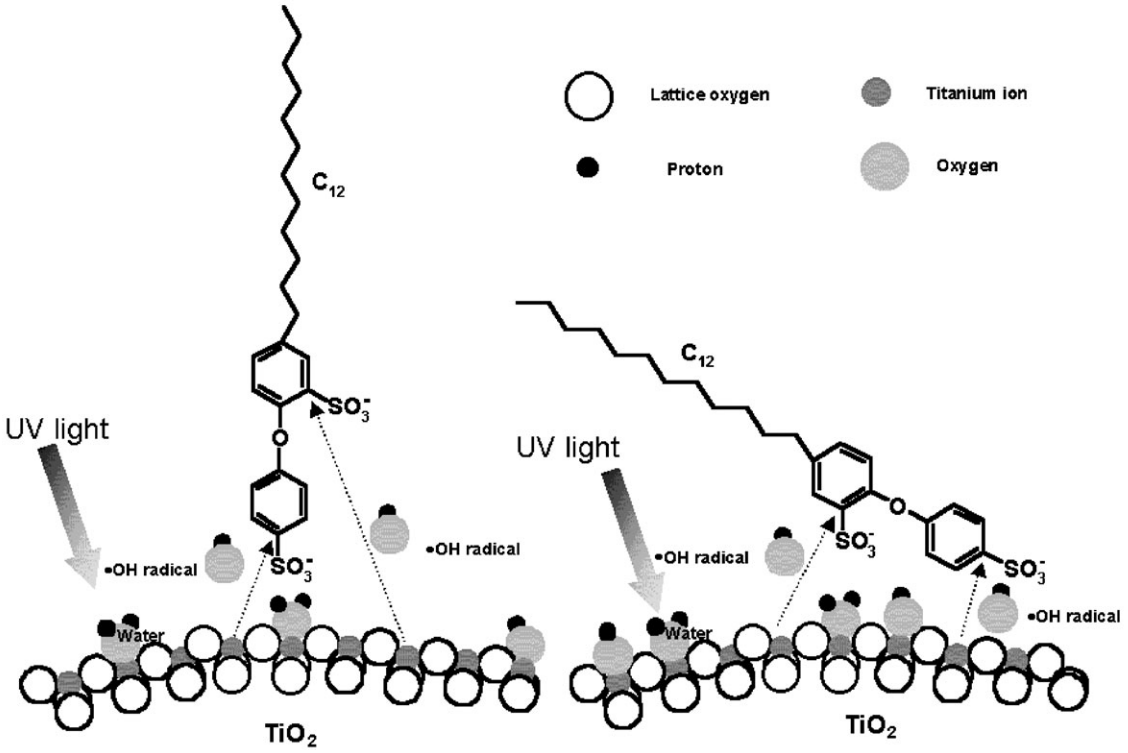


Fig. 2 Proposed adsorption modes of the disulfonated DOBS surfactant on the positively charged TiO_2 surface and the presumed $^{\bullet}OH$ radical attack at the target carbon atoms in the photocatalyzed degradation of such sulfonated surfactants in UV-irradiated aqueous TiO_2 dispersions.

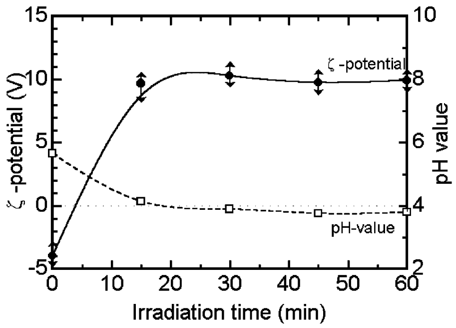


Fig. 3 Temporal changes in ζ-potential and pH changes in an aqueous TiO_2 dispersion [100 mg TiO_2 in a 0.1 mM solution (50 mL) of DOBS] *versus* irradiation time; initial pH of the aqueous DOBS solution in the TiO_2-free system was 5.80.

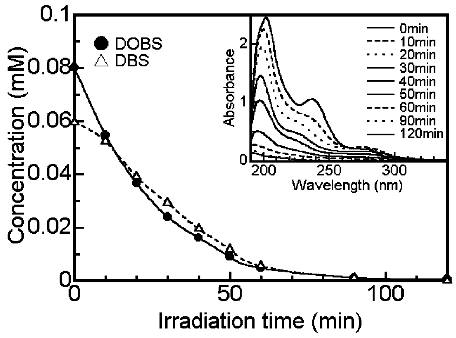


Fig. 4 Plots illustrating the first-order photocatalyzed degradation of DOBS and DBS surfactants (initial concentrations of 0.1 mM) from changes in absorption band intensities at 238 nm for DOBS (●) and at 224 nm for DBS (△). The inset shows the temporal changes of the UV spectral patterns during the photodegradation of DOBS (0.1 mM, 50 mL) at various UV irradiation times.

Pre-adsorption of substrates on the TiO_2 surface taking place during equilibration in the dark is expected to enhance the photodegradation dynamics initiated by the $^{\bullet}OH$ radicals on the TiO_2 surface.[11] The initial photoinduced cleavage of the aromatic rings of DOBS and the break-up of the aromatic ring of DBS occur through first-order kinetics; $k = 4.1 \pm 0.1 \times 10^{-2}$ min^{-1} and $3.6 \pm 0.3 \times 10^{-2}$ min^{-1}, respectively. In comparison, desulfonation of DOBS and DBS surfactants takes place at approximately the same rates and in concert with the break-up of the phenyl rings. For example, compare the data reported in Fig. 4 with the results in Fig. 7 below: *k* values for the desulfonation of DOBS and DBS are, respectively, $4.3 \pm 0.4 \times 10^{-2}$ min^{-1} and $2.8 \pm 0.3 \times 10^{-2}$ min^{-1}. It is of interest to query which phenyl group in the two-phenyl aromatic system is most likely attacked first by the $^{\bullet}OH$ (and/or $^{\bullet}OOH$) radicals. As alluded to in earlier studies,[6] these strongly oxidative radical species attack preferentially the electron-richer positions having π–π* bonds. *A priori*, the terminal phenyl ring of the DOBS structure should be attacked first through adsorption by the sulfonate group of the terminal phenyl ring, particularly if the concentration on the surface is such that the substrate is positioned perpendicular to the surface. This would then be followed by attack of the phenyl group attached to the phenyl ring bearing the hydrophobic dodecyl chain.

Temporal changes of surface tension for the photodegraded solutions at different concentrations of DOBS (0.1, 1.0, 2.5 and 5.0 mM) are depicted in Fig. 5. The initial TiO_2-free aqueous solution exhibits a lower surface tension (*ca.* 37 mN m^{-1}) than the TiO_2-dispersed solution (~64 mN m^{-1}) before irradiation. The difference between these two systems confirms adsorption of DOBS on the TiO_2 surface, in keeping with the results obtained from UV absorption (Fig. 4). A larger fraction of DOBS molecules adsorbed on the TiO_2 surface in the dilute solution (0.1 mM). At higher concentrations, this difference in surface tension between a TiO_2-free solution and a TiO_2 dispersion decreases.

From the Gibb's isotherm equation[13] the sectional area of a particle occupied by a DOBS molecule is *ca.* 0.7 nm^2. This area

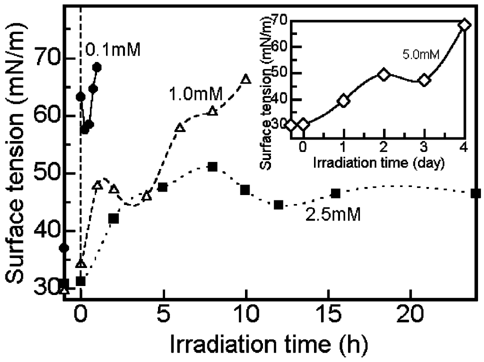


Fig. 5 Temporal changes in surface tension of degraded DOBS solutions photocatalyzed by TiO_2 particles (100 mg) at various initial concentrations of surfactant: (●) 0.1, (△) 1.0, (■) 2.5 and (◇) 5.0 mM (see inset). The c.m.c. of DOBS is 0.1 mM as determined by surface tension methods.

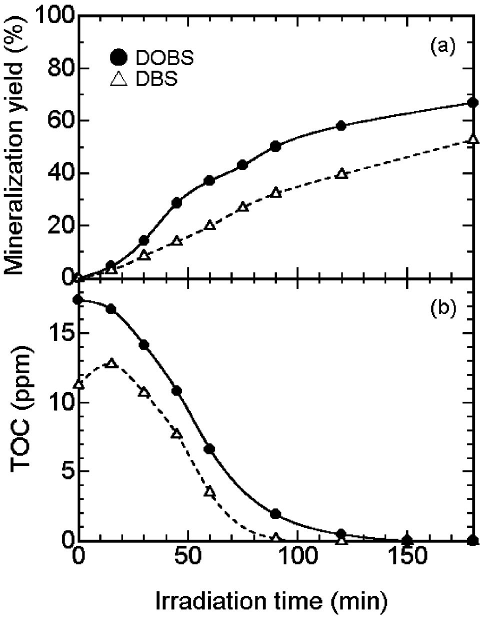


Fig. 6 (a) Mineralization yield (in terms of percent CO_2 evolved) against UV irradiation time for 50 mL solutions of 0.1 mM in DOBS (●) and DBS (△) in the presence of TiO_2 (100 mg); (b) Temporal changes in total organic carbon remaining in the solution for DOBS (●) and DBS (△) under conditions otherwise identical to those in (a).

is about 3.5 times larger than the area (0.2 nm^2) occupied by a stearic acid molecule possessing a long linear alkyl chain (taken as a reference). The surface tension of a 0.1 mM aqueous solution of DOBS increased after 1 h of UV illumination, ultimately attaining the surface tension of water (70 mN m^{-1}). For the 1.0 mM solution of DOBS (concentration greater than c.m.c.) the surface tension gradually reached *ca.* 70 mN m^{-1} with increasing irradiation time up to 10 h. The temporal behavior of the surface tension reflects the excess surface concentration of the decomposing surfactants at the H_2O/air interface. At still higher concentrations (*e.g.*, 2.5 mM), the surface tension increased and decreased during UV illumination, implying that hydrophilic and hydrophobic intermediate products are generated as transient species during the photodecomposition of the surfactant. The surface tension reflects the existence of amphiphilic intermediate photodegradated products at the air/water interface. Initially, DOBS molecules are oriented on the surface. When desulfonation occurs, the hydrophobicity of the degraded solution increases and therefore the surface tension increases. Afterwards, since the hydrophobic intermediate products are hydroxylated, hydrophilic intermediates are produced. Consequently, the surface tension is lowered. These processes are repeated to reach the surface tension of water (about 70 mN m^{-1}). Longer UV illumination times are required for the photooxidation at still higher concentrations of surfactants. For example, for a 5 mM solution 4 days were needed to reach a surface tension of *ca.* 50 mN m^{-1} (see insert to Fig. 5).

After a short induction period (15 min), the amount of CO_2 evolved in the photodegradation of DOBS and DBS (initial concentrations, 0.1 mM) increased with increasing illumination time [Fig. 6(a)]. Mineralization yields for DOBS and DBS after 3 h of UV illumination reached about 68% and 53%, respectively. Evolution of carbon dioxide also followed first-order growth kinetics; $k = 1.3 \pm 0.1 \times 10^{-2}$ min^{-1} for DOBS and 8.7 $\pm$ 1.4 $\times$ 10^{-3} min^{-1} for DBS. Clearly, CO_2 evolution is faster in the degradation of DOBS than from the DBS surfactant.

Total organic carbon assays on the aqueous degraded solutions of DOBS and DBS *versus* irradiation time are reported in Fig. 6(b). DOBS, bearing 24 equivalent carbons per molecule, exhibited a higher TOC value than DBS with only 18 carbons. The TOC concentration in aqueous DOBS solutions decreased with irradiation time after a 15 min induction period, attaining zero after *ca.* 150 min. The difference between the TiO_2-free system (23 ppm) and the TiO_2-dispersed system (18 ppm) before irradiation further points to initial adsorption of DOBS on the TiO_2 surface. The increase in TOC observed for the DBS solutions in the first 15 min of irradiation implies the photodesorption of DBS from the TiO_2 surface. After 15 min of irradiation, the decay of DBS follows first-order kinetics. The reason is found in the adsorption of DBS on the TiO_2 surface, which after *ca.* 15 min of UV illumination causes the photodesorption of DBS, which is then released into the aqueous bulk solution. The corresponding dynamics for TOC decay of DOBS are $k = 2.8 \pm 0.2 \times 10^{-2}$ min^{-1}, and for TOC decay of DBS $k = 3.7 \pm 0.5 \times 10^{-2}$ min^{-1}.

An interesting observation concerns the data of Fig. 6(a) compared to the results in Fig. 6(b). Although TOC decays to 0 ppm in a relatively short time (*ca.* 2 h), evolution of carbon dioxide appears to saturate around 75% for DOBS and around 60% for DBS. This demonstrates that some of the intermediate species produced during the photodegradative process remain adsorbed on the TiO_2 particles, since TOC is assayed subsequent to removal of the titania particles, thereby yielding a "premature mineralization" on the basis of TOC measurements. This observation is in accord with the formation of sulfate ions discussed below.

Fig. 7 depicts the generation of SO_4^{2-} ions during the degradation of DOBS and DBS surfactants for an initial concentration of 0.1 mM. Since DOBS has two sulfonate groups (SO_3^-), the amount of SO_4^{2-} ions produced should be twofold greater than that for DBS. As noted above, desulfonation occurs in concert with opening (cleavage) of the phenyl rings with formation of sulfate ions for the DOBS

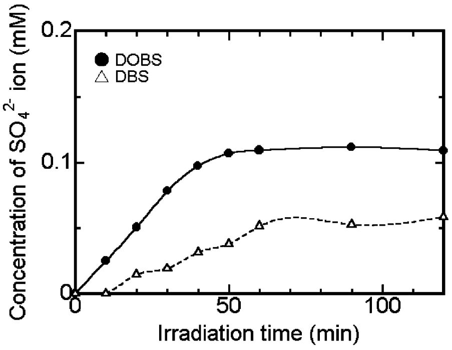


Fig. 7 Temporal formation of SO_4^{2-} ions (desulfonation) during the photodegradation of a 50 mL solution of DOBS (●) and DBS (△) at an initial concentration of 0.1 mM in the presence of TiO_2 (100 mg).

surfactant taking place approximately 1.5-fold faster than desulfonation of the monosulfonated DBS surfactant (*k* values are, respectively, $4.3 \pm 0.4 \times 10^{-2}$ min^{-1} and $2.8 \pm 0.3 \times 10^{-2}$ min^{-1}). The amount of sulfate ions in aqueous solution after removal of TiO_2 particles reached a limit of about 56% for DOBS and ~59% for DBS. The remaining quantity (*ca.* 40 to 45%) of SO_4^{2-} anions stay adsorbed on the cationically charged TiO_2 particle surface in accord with the findings of Vorontsov and coworkers,[14] who reported that monodentate sulfates on the surface of TiO_2 can be washed away, whereas bidentated sulfates remain on the particle surface and contribute to permanent catalyst deactivation. To ascertain this assertion, we carried out an experiment in which the amount of sulfate ions before and after addition of TiO_2 particles was measured at pH 5.6 in an aqueous TiO_2 (100 mg)–Na_2SO_4 (0.1 mM, 50 mL) dispersion system. About 40–50% of the sulfate ions stayed on the TiO_2 surface, with the residual *ca.* 50% SO_4^{2-} ions present in the ion-chromatographed solution. These data further substantiate the notion that the $^{\bullet}OH$ radicals attack the carbon atom bonded to the SO_3^- group in accord with results from frontier electron density calculations (see ESI and discussion above).

Proton NMR spectroscopy

The sensitivity of the NMR technique is generally poor at the low concentrations of surfactants typically examined, and this even when using an iterative scanning method. For example, we were unable to examine the oxidation processes at the lower concentrations of 0.1 and 1.0 mM. Accordingly, the initial concentration of DOBS was increased to 10.0 mM in a D_2O solution. The concentration for usual measurement NMR spectra is high. Therefore, the photocatalytic degradation required long illumination times.

Fig. 8 shows the NMR spectral patterns of a DOBS solution at different UV illumination times. The large signals in the chemical shift range $\delta = 0.5$–1.7 ppm are those of the terminal methyl and methylene protons of the dodecyl group in DOBS. These signals decreased gradually with irradiation time until *ca.* 15 h, finally disappearing at longer irradiation times of 4 days or more. Concomitantly, new peaks appeared that increased with irradiation time. They correspond to those of acetic acid ($\delta = 2.09$ ppm) and acetaldehyde ($\delta = 2.20$ ppm). The NMR signals in the $\delta = 6.7$—8.0 ppm range are those of the aromatic protons. The protons at the ortho position in the phenoxy group are seen at around 7.8 ppm, whereas those at the meta position are observed at both 7.1 and 7.3 ppm. We hasten to point out that because complex signal patterns were observed, the presence of other isomeric derivatives of DOBS in the degraded sample cannot be precluded.

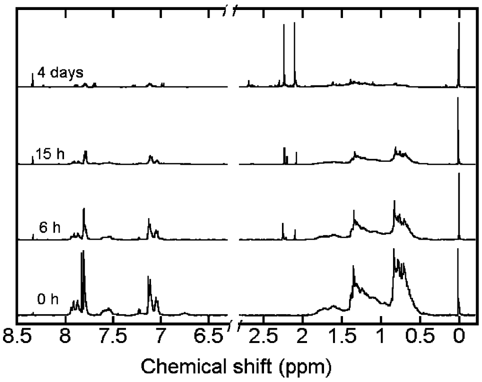


Fig. 8 Proton NMR spectral patterns recorded during the photocatalyzed degradation of DOBS (10.0 mM in a 10 mL D_2O solution) in the presence of 20 mg of TiO_2 after UV irradiation periods of 0, 6 h, 15 h and 4 days.

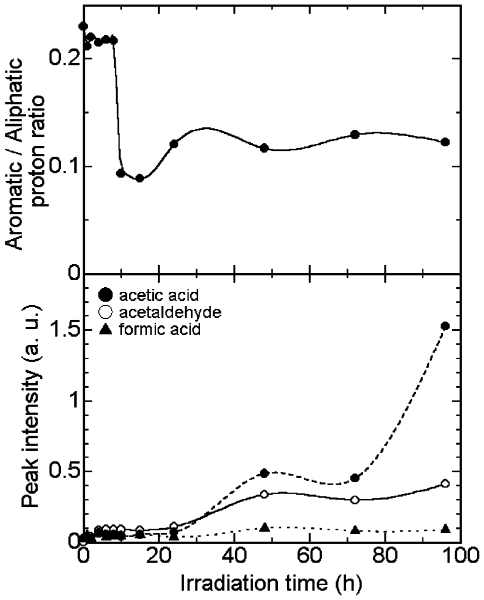


Fig. 9 (a) Temporal changes in the ratio of aromatic to aliphatic group protons during the photodegradation of a 10.0 mM solution of DOBS determined by integration of the respective proton NMR signals. (b) Temporal formation of acetic acid (●; $\delta = 2.09$ ppm), acetaldehyde (O; $\delta = 2.20$ ppm), and formic acid (▲; $\delta = 8.25$ ppm) assayed by integration of the corresponding NMR signals during the photocatalyzed degradation of a 10.0 mM solution of DOBS surfactant.

The ratio of aromatic protons (seven) to aliphatic protons (twenty-five) in the alkyl chain obtained by integration of the relevant NMR signals for the oxidatively degraded DOBS solution (10.0 mM) is presented in Fig. 9(a). Initially, the ratio stayed fairly constant for *ca.* 10 h, after which the ratio decreased rapidly to remain nearly constant with continued irradiation. The temporal formation of acetic acid ($\delta = 2.09$ ppm), acetaldehyde ($\delta = 2.20$ ppm), and formic acid ($\delta = 8.25$ ppm) intermediates was confirmed by peak intensity integration of the H^1-NMR spectra [Fig. 9(b)]. After an induction period of about 24 h, the relative quantities of these intermediates after 4 days of irradiation followed the order: acetic acid (1.0) > acetaldehyde (0.27) > formic acid (0.06).

Comparison of the integrated aromatic peaks seen in the range 7.0–8.0 ppm with those NMR features of the long alkyl chain(s) observed in the range 0.4–1.9 ppm indicates that the benzene rings in DOBS degrade faster than the longer methylene chains, at least for up to 8 h of UV irradiation (not shown in Fig. 8). This adds further credence that the $^{\bullet}OH$ radicals photogenerated on the TiO_2 surface preferentially attack the electron-rich benzene moieties, bearing π-π^* bonds to produce $^{\bullet}OH$-adducts, relative to the alkyl dodecyl chain, which requires much longer illumination times to degrade because of the relatively slower H-abstraction reaction dynamics involving $^{\bullet}OH$ radicals with aliphatics (*e.g.*, $k = 1.7 \times 10^{10}$ M^{-1} s^{-1} for adduct formation of $^{\bullet}OH$ radicals with benzene,[15] whereas reaction of these radicals with 2-bromobutane[16] is about two orders of magnitude slower: $k = 1.5 \times 10^{8}$ M^{-1} s^{-1}). The OH radicals represent an electrophilic function. Therefore the OH radicals tend to attack an electrophilic group bearing the π-π^* bond, although we do recognize that the π-π^* bonds are not localized in the phenyl ring.

Concluding remarks

Some major conclusions can be inferred from the present study on the titania photocatalyzed mineralization of alkylated benzene-sulfonate surfactants. (a) Desulfonation occurs in concert with opening (cleavage) of the phenyl groups, (b) a significant fraction of sulfate ions produced remain on the photocatalyst surface [bidentate bound to Ti(IV) surface ions], potentially deactivating it, (c) the phenyl rings degrade faster than the aliphatic dodecyl chain(s) to yield acetic acid, acetaldehyde and formic acid on their way to carbon dioxide, and (d) the sulfonated substrates examined here lend further support to the notion that the mode of adsorption of substrates does play a not insignificant role in the TiO_2 mediated photodegradative process.

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