Photocatalytic Degradation of Surfactants. XX. Photooxidation of Sodium Butylnaphthalenesulfonates

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Abstract: The photocatalyzed degradation of surface-active and surface-inactive naphthalene-sulfonate derivatives has been investigated in UV-irradiated air-equilibrated heterogeneous TiO2 dispersions. The dynamics for the photodegradation of sodium butylnaphthalene-1-sulfonate (B-1-NS) and sodium naphthalene-1-sulfonate (1-NS) are compared to those of sodium dodecylbenzenesulfonate (DBS) and sodium benzenesulfonate (BS). The adsorption behavior of the surfactants on the TiO2 catalyst, cleavage of the aromatic ring, mineralization to carbon dioxide, formation of sulfate ions, and the temporal changes of the surface activity (surface tension) against UV irradiation time were probed experimentally to provide inferences on the photoinitiated mechanism. The position(s) of ·OH and/or ·OOH radicals attack on the surfactant structure was inferred from theoretical considerations on the basis of molecular orbital calculations of frontier electron densities; similarly, the adsorption behavior of the surfactants on the TiO2 catalyst surface was deduced from calculations of point charges of each of the atoms in the surfactant structure.

Key words: photodegradation, photooxidation, titanium dioxide, photocatalyst, butylnaphthalenesulfonate

1 Introduction

To our knowledge, the first study to report the photocatalyzed oxidation of an organic substance was that of Kato and Mashio in 1964 (1), who examined the degradation of tetrabenzene. In our laboratories, we have extensively investigated the photocatalytic decomposition of anionic surfactants bearing a sulfonate or a sulfonated aromatic moiety to assess the relationship(s) between chemical structure and degradation dynamics (2-6). Germane to the present study, the photocatalyzed oxidation of polyaromatic hydrocarbon substances such as naphthalene (7-9) and anthracene (10) has also been examined in aqueous TiO2 dispersions. Naphthalene is degraded photocatalytically in aqueous media in the presence of TiO2 catalyst to generate (E, Z)-2-formylcinnamaldehydes and 1, 4-naphthoquinone, in addition to traces of naphthols (11). In the presence of H2O2 (6%) in acetonitrile/H2O solutions, the process generates 1,3-, 1,4- and 1,8-dihydroxynaphthalenes (12, 13). Photocatalyzed oxidations of other polyaromatic hydrocarbons, namely 1- and 2-methylphenanthrenes (14), and anthracene-1-sulfonate (15) have also been reported.

Sodium butylnaphthalenesulfonate (BNS) is a widely used direct homogenizing wetting agent for acidic dyes. It is also employed as a permeating agent and as a dispersant. Treatment methods to detoxify wastewaters...
containing these non-biodegradable BNS systems are required to achieve aquatic remediation. Hydroxyl (·OH) and/or peroxyl (·OOH) radical species generated in aqueous solutions of UV-illuminated TiO₂ dispersions in atmosphere air (or oxygen gas) possess strong oxidative powers. Which were evidenced by the ESR spin-trapping technique using the 5,5-dimethyl-1-pyroline-N-oxide (DMPO) agent as published before (3). Generally, ·OH and/or ·OOH radicals are non-selective toward the destruction of various organics and metal-organic ions in aqueous solutions. However, positions of initial attack of ·OH and/or ·OOH radicals on an organic substrate are an important parameter in deducing overall mechanistic events. As well, another parameter that affects the photodegradation kinetics is the adsorption behavior of the substrate on the TiO₂ catalyst surface.

In this paper, we compare the photodegradation behaviors of surface-active and surface-inactive naphthalenesulfonates with those of benzenesulfonates. The positions of attack of ·OH and/or ·OOH radicals on the chemical structure of the naphthalenesulfonates were assessed theoretically by frontier electron density calculations. Adsorption behaviors of the surfactants on the TiO₂ surface were estimated from point charge calculations.

2 Experimental Section

2·1 Materials

The commercial brownish reagents (about 10 g) containing about 35% of sodium butynaphthalene-1-sulfonate (B-1-NS) and sodium dibutynaphthalene-1-sulfonate (DB-1-NS) were available commercially (PELEX NBL, Kao Corporation, Japan). Solutions of the surfactants in the mixed solvents ethanol/water (50/50 v/v%) were purified (decolorization) using activated carbon powders at 40°C, followed by filtration to remove these carbon powders. A freeze-dry method was employed to obtain the tested samples of the B-1-NS/DB-1-NS mixture, now containing ca. 55% B-1-NS and ca. 44% DB-1-NS as determined by mass spectral analysis of the negative fragments using an Agilent 1100 LC/MSD liquid chromatograph-mass spectrometer. The sodium naphthalene-1-sulfonate (1-NS), sodium benzenesulfonate (BS) and sodium dodecylbenzenesulfonate (DBS) surfactants were employed without purification as supplied by Tokyo Kasei. Ind. Co. Ltd. Titanium dioxide was Degussa P-25 TiO₂ (surface area, 53 m² g⁻¹ by BET; particle size, 20 to 30 nm as observed by transmission electron microscopy; crystallinity was 83% anatase and 17% rutile as determined by X-ray diffraction).

2·2 Procedures

A 50-mL aqueous dispersion consisting of the test substrate (0.1 mM) and TiO₂ particles (100 mg) was placed in a 124-mL Pyrex vessel. The headspace volume in the reaction vessel was fully purged with oxygen for about 20 min prior to UV irradiation. The mixture was dispersed by sonication for ca. 5 min, and then illuminated with a Toshiba SQ100-75W mercury lamp (2.7 mW cm⁻² at 360 nm) under continuous magnetic agitation.

The 50-mL dispersion was illuminated for 10, 20, 30, 40, 50, 60, 90 and 120 min. At each of these various times, the irradiated dispersion was sampled and then followed by removal of the TiO₂ catalyst by centrifugation and/or filtration. After removal of the TiO₂ catalyst, the surface tension of the degraded solutions was measured at ambient temperature with a Wilhelmy surface tensiometer (Kyowa Interface Science Co. Ltd., CBVP-Z type). A Shimadzu GC-8A gas chromatograph equipped with a TCD detector and a Porapack Q column monitored evolution of CO₂; helium was the carrier gas. The concentrations of SO₄²⁻ ions were monitored on a JASCO ion chromatograph equipped with an I-524 anionic column and a CD-5 conductivity detector. UV absorption spectra were recorded on the JASCO V-570 spectrophotometer. The H¹-NMR spectra were obtained on a JEOL JNM-AL300 spectrometer (300-MHz) in D₂O solution using the 3-(trimethylsilyl)propionic-2, 2, 3, 3-d₄ acid sodium salt as the standard agent enclosed in a capillary tube. The peak intensity of each proton signal of the sodium naphthalene-1-sulfonate (1-NS) surfactant was normalized against the proton signal at 0 ppm of the standard agent. The relative ratios were plotted against irradiation time.

2·3 Calculations

Computer simulations were performed using the WinMOPAC 3.0 system (Fujitsu, 2000) to calculate the frontier electron densities and to assess the positions of attack of ·OH and/or ·OOH radicals on the surfactant structure, and to estimate the point charges of all the atoms in the naphthalenesulfonate sodium salts to deter-
mine the adsorption behaviors of the surfactants on the TiO$_2$ surface. These were followed by optimization of the geometric calculations using MOPAC and PM3 parameters; the calculations included solvation effects simulated using the COSMO software (16, 17).

3 Results and Discussion

The temporal UV spectral changes occurring during the photodegradation of B-1-NS/DB-1-NS (henceforth referred to as BNS), 1-NS, DBS and BS surfactants at different irradiation times are shown in Fig. 1. The UV bands (274 nm and 228 nm) corresponding to the naphthyl moiety decreased significantly with irradiation time accompanied by the appearance of a broad band around 200-210 nm for the naphthylsulfonates. The latter feature implies that one of the benzene rings of BNS and 1-NS was cleaved. In comparison, the band intensity at 212 nm for BS decreased with increasing UV illumination time. The cleavage of the aromatic ring likely results from attack of the substrate by the strongly oxidative ·OH and/or ·OOH radical species. Similarly, the phenyl band (224 nm) of the DBS surfactant decreased with time. Evidently, the naphthyl moiety of the BNS and 1-NS surfactants degraded within about 30 min of UV-irradiation, whereas the phenyl moiety of BS did so within ~60 min and that of DBS within 120 min. It appears that attack by the oxidative ·OH and/or ·OOH radical species on the naphthyl moiety is more extensive than that on the lone phenyl ring of BS and DBS. This experimental result suggests that ·OH and/or ·OOH radicals attack preferentially the more electron-rich groups having π-π$^*$ bonds.

The temporal changes in concentration of the photodegraded solutions (0.1 mM) against UV-irradiation times are depicted in Fig. 2. Adsorption of the surfactant on the TiO$_2$ surface increased in the following order: BS < 1-NS < BNS < DBS. The data indicate that the BS surfactant is present mostly in the aqueous bulk solution (i.e., 0% for static adsorption), whereas DBS is adsorbed in an approximately 40% ratio on the TiO$_2$ surface, and BNS is also done in a ca. 20% ratio. It must be noted that the DBS surfactant adsorbed on TiO$_2$ is in adsorption equilibrium with that in bulk solution.

**Fig. 1** Temporal UV Spectral Changes Occurring during the Photodegradation of BNS, 1-NS, BS and DBS (0.1 mM, 50 mL) in the Presence of the TiO$_2$ Catalyst (100 mg). The Illumination Times were 0, 10, 20, 30, 40, 50, 60, 90, and 120 min.

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Some of the DBS surfactant in bulk solution appears to absorb on illumination, followed by cleavage of the aromatic ring and then the degraded intermediates are transferred into the bulk solution. With regard to 1-NS and BNS, the benzene ring having no sulfonate group in the naphthyl structure would appear to be cleaved via hydroxylation through attack by \( \cdot \text{OH} \) and/or \( \cdot \text{OOH} \) radicals. Subsequently, the benzene ring having the sulfonate function would be mineralized to \( \text{CO}_2 \) gas.

The temporal changes in surface tension for the photodegraded BNS solution at different concentrations are displayed in Fig. 3. The surface tension for the most dilute solution of 0.1 mM is the same (72 mN m\(^{-1}\)) before and after UV irradiation. At the higher concentration of 1 mM, the surface tension of the BNS solution changed from an initial 54 mN m\(^{-1}\) to 72 mN m\(^{-1}\) after 7 h of irradiation. By contrast, the surface tension of the 2.5 mM solution increased gradually with irradiation time from ca. 42 mN m\(^{-1}\) to reach 71 mN m\(^{-1}\) after 16 h. At the highest concentration (10 mM) examined above the critical micelle concentration, 2 d of irradiation were needed to attain a surface tension of 70 mN m\(^{-1}\) from an initial 35 mN m\(^{-1}\).

The temporal formation of sulfate ions taking place during the photodecomposition of BNS, 1-NS, DBS and BS (0.1 mM, 50 mL) is shown in Fig. 4. Initial desulfonation occurred rapidly during the first 30 to 40 min. After 50 min of UV irradiation, the extent of generation of sulfate ions decreased in the following order: BS > 1-NS ~ BNS > DBS. Such relatively fast desulfonation implies that the \( \cdot \text{OH} \) and/or \( \cdot \text{OOH} \) radicals preferentially attack the C\(_1\) carbon bonded to the sulfonate group (see also below).

Because of the effective formation of hydroxyl radicals, strongly oxidizing conditions are generated in the irradiated oxygenated TiO\(_2\) dispersions enabling ultimately the total mineralization of various organics. Figure 5 shows the extent of the photocatalyzed mineral-
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The relative rates of mineralization are in the order BS > 1-NS > BNS > DBS for ca. 1.5 h of UV illumination. The CO₂ mineralization yields indicate that about 80-85% of 1-NS and BS, ca. 60% of BNS, and about 50% of DBS are photocatalytically mineralized after 3 h of exposure to UV radiation.

To get a handle on some of the mechanistic events occurring during the photodegradation, calculations were carried out using molecular orbital methods to estimate frontier electron densities and point charges on each of the atoms of the naphthalenesulfonate derivatives. The relevant data for sodium naphthalene-1-sulfonate (1-NS) and for the butyl derivatives are listed in Table 1; the data for sodium dibutynaphthalene-1-sulfonate derivatives (DB-1-NS) are summarized in Table 2. Determination of which atom(s) carries the largest negative point charge provides some indication as to the direction of approach of the naphthyl skeleton toward the catalyst surface, and to the ultimate point of adsorption of the naphthalenesulfonates on the positively charged TiO₂ particle surface in acidic aqueous media (pH below 6.3). Since the sulfonate (-SO₃⁻) oxygens are the most negatively charged atoms, it is clear that the major point of contact between the positively charged TiO₂ surface and the anionic naphthalenesulfonate species is the sulfonate function.

In general, the reactivity of ·OH and/or ·OOH radicals is rather non-selective. These radicals attack all substrates coexisting in the aqueous bulk solution. However, the point of attack on a substrate depends on the electron densities of the atoms in the structure of the substrate since the ·OH and/or ·OOH radicals are strongly electrophilic. The C₁ carbon atom bonded to the sulfonate group bears the highest electron density (Table 1). Accordingly, the C₁ atom is expected to be the first to be attacked by the ·OH and/or ·OOH radicals. Evidence in support of this inference originates with the relatively rapid formation of sulfate ions (Fig. 4). In the time scale of the total photodegradation, the sulfate ion is formed in an early step in the overall mechanism before the formation of the various oxidative intermediates such as aldehydes, carboxylic acids, carbon dioxide, and others.

On the basis of the electron density data listed in Table 1 for 1-NS, the electrophilic ·OH and/or ·OOH radicals should attack the carbon atoms in the following order: C₁ (4.487) > C₃ (4.156) > C₁₀ (4.148) > C₈ (4.138) > C₄ (4.102) > C₉ (4.098) > C₇ (4.097) > C₄ (4.049) > C₆ (3.980) > C₃ (3.971). Since the most electron-rich position is the C₁ carbon, the ·OH and/or ·OOH radicals are expected to attack this carbon and convert the surfactant to a hydroxyl derivative, followed by the rapid formation of SO₄²⁻ ions. Attack of ·OH and/or ·OOH radicals on the C₃ and C₆ carbons should be attenuated somewhat. Results of electron density calculations suggest three possible isomers for the butynaphthalene-1-sulfonates; they are 3-butylnaphthalene-1-sulfonate (3-B-1-NS), 8-butylnaphthalene-1-sulfonate (8-B-1-NS), and 10-butylnaphthalene-1-sulfonate (10-B-1-NS) - see Table 1. Similarly, the dibutyl derivatives also display three possible structures: 3,8-dibutylnaphthalene-1-sulfonate (3,8-DB-1-NS), 8,10-dibutylnaphthalene-1-sulfonate (8,10-DB-1-NS), and 3,10-dibutylnaphthalene-1-sulfonate (3,10-DB-1-NS) - see Table 2. After the photodegradation of the organic substrates, the aqueous TiO₂ dispersions become acidic because of
formation of protons and $\cdot$OH and/or $\cdot$OOH radicals; the surface potential is positive from experimental results of $\zeta$-potential measurements. Accordingly, the atoms having a negative point charge will preferentially adsorb on the surface of TiO$_2$ particles. As noted above, the sulfonate oxygens are chemisorbed on the TiO$_2$ catalyst surface.

The temporal NMR spectral patterns in the photocatalytic degradation of the naphthalene skeleton in 1-NS (1 mM D$_2$O solution) are shown in Fig. 6. The protons in 1-NS were identified by two-dimensional NMR techniques. The relevant proton chemical shifts are: C$_2$H 8.16, 8.14 ppm; C$_3$H 7.62, 7.59 ppm; C$_4$H 8.08 ppm; C$_5$H 8.06 ppm; C$_6$H 7.70, 7.68, 7.64 ppm; C$_7$H 7.75, 7.73, 7.77 ppm; C$_8$H 8.66, 8.63 ppm. Each proton signal decreased gradually with increasing illumination time. All NMR signals disappeared within about 2 h. The skeleton of 1-NS (1mM) degraded following attack
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In general, the highly electrophilic ·OH and/or ·OOH radicals will attack the atom possessing the highest electron density. The position of attack by the ·OH and/or ·OOH radical species was inferred from simulations of electron densities, without consideration of the adsorption factor (as judged by point charges) on the TiO$_2$ surface.

Although the electron density at the C$_2$H carbon is the lowest among other carbons, the disappearance of the proton signals at 8.16 ppm and 8.14 ppm is nonetheless remarkable (Figs. 7a and 7b). The likely cause of this is the relatively strong adsorption of 1-NS on the positively charged TiO$_2$ surface, as estimated from point charge calculations (see Table 1). The distance between the C$_2$ carbon atom and the ·OH and/or ·OOH radicals generated on the irradiated TiO$_2$ surface is relatively short. The proton peaks belonging to the C$_3$ and C$_8$ carbon atoms also decreased with irradiation time. Hydroxyl radical attack on these two carbon atoms will also yield hydroxylated naphthalene derivatives. The overall results indicate that competitive oxidation reactions likely occur to yield complex intermediate products (not identified in this study). Interestingly, temporal changes in the ratios of proton signal intensities of the hydrogens bonded to the C$_9$ and C$_{10}$ carbons were rather minor (Fig. 7b).

In summary, we conclude that the initial oxidative process, namely cleavage of the naphthalene ring, pro-

| 3,8-dibutyl naphthalene-1-
sulfonate (3,8-DB-1-NS) | 8,10-dibutyl naphthalene-1-
sulfonate (8,10-DB-1-NS) | 3,10-dibutyl naphthalene-1-
sulfonate (3,10-DB-1-NS) |
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Table 2  Calculated Data of Frontier Electron Densities and Point Charges for Dibutyl Derivatives of Sodium Naphthalene-1-Sulfonate.

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Although the electron density at the C$_2$H carbon is the lowest among other carbons, the disappearance of the proton signals at 8.16 ppm and 8.14 ppm is nonetheless remarkable (Figs. 7a and 7b). The likely cause of this is the relatively strong adsorption of 1-NS on the positively charged TiO$_2$ surface, as estimated from point charge calculations (see Table 1). The distance between the C$_2$ carbon atom and the ·OH and/or ·OOH radicals generated on the irradiated TiO$_2$ surface is relatively short. The proton peaks belonging to the C$_3$ and C$_8$ carbon atoms also decreased with irradiation time. Hydroxyl radical attack on these two carbon atoms will also yield hydroxylated naphthalene derivatives. The overall results indicate that competitive oxidation reactions likely occur to yield complex intermediate products (not identified in this study). Interestingly, temporal changes in the ratios of proton signal intensities of the hydrogens bonded to the C$_9$ and C$_{10}$ carbons were rather minor (Fig. 7b).

In summary, we conclude that the initial oxidative process, namely cleavage of the naphthalene ring, pro-

ceeds via hydroxylation of the aromatic carbons through attack by \( \cdot \)OH and/or \( \cdot \)OOH radicals. The identification of electron-rich carbon atoms by computer simulations provides a useful indication on the initial events into an otherwise complex sequence in the decomposition of organic chemical structures.

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**References**

2. H. HIDAKA, H. KUBOTA, M. GRÄTZEL, N. SERPONE and E. PELIZZETTI, Photodegradation of Surfactants I: Degradation of Sodium Dodecylbenzene Sulfonate in Aqueous Semi-
Photooxidation of Sodium Butynaphthalenesulfonates


