ORIGINAL

Photodegradation of Surfactants. III.

Heterogeneous Photocatalytic Degradation of Cationic Surfactants on TiO₂ Particles

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The heterogeneous photocatalytic degradation of cationic surfactants including benzyldecyl=dimethyl ammonium chloride (BDDAC) was carried out in the presence of oxygen with powdery TiO₂ suspended. The surface activity was lowered with irradiation time. The long alkyl chain and aromatic moiety in BDDAC were competitively degraded.

The photocatalytic decomposition rate of BDDAC was faster in a neutral than an acidic or alkaline medium.

1 Introduction

Chlorine-containing organic chemicals cause serious environmental problems owing to their toxicity and widespread utilization. Since these chemicals are not biodegradable, a photocatalytic process may provide an effective means for their decomposition.

Photodecomposition of haloaromatics such as chlorobenzene^{1)~3)}, chlorophenol^{4),5)}, and polychlorinated biphenyl (PCB)⁶⁾ has been already reported. Further, halogenated organic solvents such as trichloroethylene, dichloroethane, and chloroform, which are widely used in the fields of advanced technology (*e.g.* IC fabrication), were photodegraded to non-toxic CO₂ and HCl by heterogeneous photocatalytic oxidation^{7),8)}. Concerning surfactants which are predominant wastewater contaminants, to our knowledge there has been no research except on the photodegradation of sodium dodecylbenzene sulfonate^{9)~11)}. Cationic surfactants of common use undergo slow biodegradation because of their bactericidal activity, and they are more toxic to animals and plants than

other kinds of surfactants^{12),13)}. In ecological points of view, a complete wastewater treatment is urgently required.

This paper describes effective decomposition of cationic surfactants by semiconductor photocatalysis.

2 Experimental

Reagent-grade benzyldecyldimethylammonium chloride [BDDAC; CH₃(CH₂)₁₁N⁺(CH₃)₂=CH₂C₆H₅Cl⁻], benzyltrimethylammonium chloride [BTAC; C₆H₅CH₂N⁺(CH₃)₃Cl⁻], and hexadecyltrimethylammonium bromide [HDTAB; C₁₆H₃₃N⁺(CH₃)₃Br⁻], were used as supplied from Wako Pure Chem. Ind., Ltd.

Deionized water was used after distillation. As an *n*-type semiconductor photocatalyst, powdery TiO₂ (Degussa P25, mostly anatase, surface area 55 m²·g⁻¹) was employed. A 25-mL aerated or oxygenated aqueous solution of BDDAC, BTAC, or HTAB (50 ppm) with 50 mg of suspended TiO₂ was irradiated with a 500-W xenon lamp (Ushio Inc.) in a Pyrex reaction vessel (37 mL) under magnetic stirring at about 37°C. After photolysis, the slurry was centrifuged with a Hitachi centrifuge

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(Model SCT-4BD) for at least 20 min and then filtered with a millipore SJGV 013 NS filter (pore size $0.22\ \mu\text{m}$), and the spectral changes were monitored with a JASCO spectrophotometer (Model UVIDE-660).

The concentrations of BDDAC and BTAC were determined spectrophotometrically at either 208.0 nm or 262.4 nm.

Major intermediates in the photodegradation were identified with a Hitachi NMR spectrophotometer (Model R-22, 90 MHz). In order to prevent the pH effect, a capillary containing a D_2O solution of sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) as a reference was placed in a sample tube. The D_2O solution of BDDAC (2 wt%) was adjusted to pH 10.0 with NaOD (Merck) or to pH 4.0 with DCl (Merck) with a micro pH-electrode. The surface tension of the solutions, after removal of TiO_2 particles by centrifuging (>10 min) followed by filtration, was measured at ambient temperature by a Whilhelmy's vertical plate method with a Shimadzu tensiometer (Model ST-1).

3 Results and Discussion

Time courses for the surface tension of BDDAC solutions during photolysis are shown in Fig.-1 as a function of BDDAC concentra-

Fig.-1 Temporal evolution of surface tension, reflecting photodegradation of BDDAC under xenon lamp illumination (>330 nm).

tion.

At a concentration of 50 ppm, which is well below the cmc, BDDAC was decomposed within 2 h. At higher concentrations, the decomposition of BDDAC was slower. Above the cmc, *i.e.* at 3000 ppm, the surface tension did not change until 3 h irradiation, and a longer irradiation time was required for complete degradation. The foam caused by stirring the BDDAC solution (50 ppm) during photolysis disappeared after 30 min irradiation.

Fig.-2 Same as Fig.-1 but for HDTAB.

Table-1 pH Dependence of degradation half-life period*.

	Initial pH	Final pH**	Degradation half-life $t_{1/2}$ (min)
BDDAC	1.6	1.8	180
	2.6	3.3	75
	4.0	4.0	50
	6.0	4.8	35
	6.8	5.4	25
	6.8	5.6	30
	7.0	5.2	25
	8.0	5.8	35
	10.2	6.3	50
	12.0	8.5	260
BTAC	3.6	4.2	30
	6.8	5.4	14
	10.4	6.3	17

* BDDAC or BTAC solutions (50ppm, 25 mL) were photodegraded with 50 mg of TiO_2 by xenon lamp illumination (>330 nm).

** The pH value after 5 h irradiation.

A similar plot for the photodegradation of HDTAB is illustrated in **Fig.-2**.

At 50 ppm, HDTAB was degraded in 4 h of irradiation. The degradation of HDTAB was very slow at concentrations above the cmc (279 ppm). In contrast to BDDAC, HDTAB does not possess an aromatic moiety. The aromatic group hence appears to be a 'target' for photo-degradation.

The pH dependence of degradation half-life for the aromatic moiety of BDDAC and BTAC is given in **Table-1**.

The decomposition of BDDAC having a long alkyl chain is slower than that of BTAC. The decomposition half-life periods for both BDDAC and BTAC are shorter in neutral medium than in acidic and alkaline media. TiO_2 has an amphoteric property with the isoelectric point (pI) of 5.3, to which the pH value during photolysis gradually approaches.

Since the TiO_2 surface in an acidic medium possesses positively charged $-\text{OH}_2^+$ groups, the cationic BDDAC is repelled and therefore the decomposition is slowed. On the other hand, the TiO_2 surface is negatively charged in an alkaline medium due to the presence of $-\text{O}^-$. The BDDAC surfactant cations must be strongly adsorbed on the negative TiO_2 surface by coulombic interaction. Hence the attack of more reactive $\cdot\text{OH}$ radical, formed *via* the formation of electron-hole, to the aromatic group is lowered. Consequently, the catalytic action of TiO_2 is weakened in an alkaline medium.

● : in the absence of TiO_2 , □ : 10 mg TiO_2 /25 mL
○ : 50 mg TiO_2 /25 mL, △ : 100 mg TiO_2 /25 mL
Fig.-3 Effect of the amount of TiO_2 catalysis on the photodegradation rate of BDDAC.

Fig.-4 NMR spectral evolution during BDDAC (2 wt%) photodegradation at pH=7.0

The effect of the amount of TiO_2 on the BDDAC degradation rate (50 ppm, 25 mL) is shown in **Fig.-3**.

In the absence of the catalyst, BDDAC is slowly photodegraded and about 48 h irradiation is required for attaining 95% degradation. In fact, a further increase of the TiO_2 content (100 mg or 200 mg) did not increase significantly the degradation rate. Light scattering by the turbid suspension may be one possible cause for this.

The presence of the catalyst and UV light is essential for rapid degradation of the surfactants. Oxygen and water are also important ingredients for the photodegradation process, as confirmed by blank experiments.

The MMR spectra of BDDAC (2% D_2O solution) for different irradiation times are illustrated in **Fig-4**.

In the initial stage, both the methylene peak (1.25 ppm) and the aromatic peak (7.43 ppm) were gradually declined. A new peak (7.55 ppm) assignable to the aromatic moiety arose accompanying photodegradation. This would reflect oxidation of the aromatic moiety to form hydroxy aromatics.

By further irradiation, the terminal methyl group (0.87 ppm), and the dimethyl group adjacent to the ammonium cation (3.02 ppm) were slowly decomposed.

Consequently, the oxidation of benzene moiety and alkyl chain occurred competitively. Similar behaviors were noted in both alkaline and acidic media.

Although a detailed mechanism for photodecomposition cannot be deduced from the pre-

sent data, we speculate, referring to the published results on the similar systems, the photo-oxidation mechanism as follows¹⁴⁾⁻¹⁶⁾. Light absorption by TiO_2 created electron/hole pairs. The holes are subsequently trapped by surface hydroxyl groups yielding adsorbed $\cdot\text{OH}$ radicals. Alternatively, direct hole scavenging by the aromatic group in BDDAC adsorbed on the TiO_2 surface could occur. These $\cdot\text{OH}$ radicals, which are very reactive, attack the aromatic group to yield hydroxycyclohexadienyl radicals, and the radicals are further oxidized.

To summarize, cationic surfactants can be efficiently photodegraded in the presence of oxygen with TiO_2 aqueous suspensions. The surface activity was lowered by ultraviolet irradiation. The long alkyl chain and the aromatic moiety in the surfactants were competitively decomposed.

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界面活性剤の光分解 (第3報)

酸化チタンを用いる カチオン界面活性剤の不均一系光触媒的分解

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カチオン界面活性剤ベンジルドデシルジメチルアンモニウムクロリド (BDDAC) を、不均一系光触媒 TiO_2 を用い、酸素存在下で光分解した。表面張力が時間と共に低下した。BDDAC の長鎖部分と芳香基部分が競争的に分解した。中性領域の方が酸またはアルカリ領域より分解速度は速い。