Photodegradation of Surfactants. III.
Heterogeneous Photocatalytic Degradation of Cationic Surfactants on TiO$_2$ Particles

Hisao Hidaka*, Yasuji Fujita*, Kazuya Ibara*, Shinya Yamada*,
Keiichi Suzuki*, Nick Serpone**, and Ezio Pelizzetti***

* Department of Chemistry, Meisei University
(2-1-1, Hodokubo, Hino-shi, Tokyo 191)
** Department of Chemistry, Concordia University
(1455 de Maisonneuve Blvd., West Montreal, Quebec H3G 1M8, Canada)
*** Dipartimento di Chimica Analitica, Universita di Torino,
(5, Via Pietro Giuria, Torino 10125, Italy)

The heterogeneous photocatalytic degradation of cationic surfactants including benzyldodecyl- dimethyl ammonium chloride (BDDAC) was carried out in the presence of oxygen with powdery TiO$_2$ 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$^{13-14}$, chlorophenol$^{15,16}$, and polychlorinated biphenyl (PCB)$^{17}$ 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 CO$_2$ and HCl by heterogeneous photocatalytic oxidation$^{18,19}$. Concerning surfactants which are predominant wastewater contaminants, to our knowledge there has been no research except on the photodegradation of sodium dodecylbenzene sulfonate$^{20-21}$. 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$^{22,23}$. 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 benzyldodecyl(dimethylammonium chloride[BDDAC; CH$_3$(CH$_2$)$_{11}$N(CH$_3$)$_2$CH$_2$C$_6$H$_5$Cl$^-$], benzyltrimethylammonium chloride [BTAC; C$_6$H$_5$CH$_2$N(CH$_3$)$_3$Cl$^-$], and hexadecyltrimethylammonium bromide [HDTAB; C$_{16}$H$_{33}$N(CH$_3$)$_3$Br$^-$], were used as supplied from Wako Pure Chem. Ind., Ltd.

Deionized water was used after distillation. As an n-type semiconductor photocatalyst, powdery TiO$_2$ (Degussa P25, mostly anatase, surface area 55 m$^2$·g$^{-1}$) was employed. A 25-mL aerated or oxygenated aqueous solution of BDDAC, BTAC, or HTAB (50 ppm) with 50 mg of suspended TiO$_2$ 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.
(Model SCT-4BD) for at least 20 min and then filtered with a millipore SJGV 013 NS filter (pore size 0.22 μm), and the spectral changes were monitored with a JASCO spectrophotometer (Model UVISPEC-600).

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 D₂O solution of sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) as a reference was placed in a sample tube. The D₂O solution of BDDAC (2 wt%) was adjusted to pH 10.0 with NaOD (Merck) or to pH 4.0 with DCI (Merck) with a micro pH-electrode. The surface tension of the solutions, after removal of TiO₂ particles by centrifuging (>10 min) followed by filtration, was measured at ambient temperature by a Wilhelmy’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 concentration.

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.

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

<table>
<thead>
<tr>
<th></th>
<th>Initial pH</th>
<th>Final pH**</th>
<th>Degradation half-life t₁/₂ (min)</th>
</tr>
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<tbody>
<tr>
<td>BDDAC</td>
<td>1.6</td>
<td>1.8</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
<td>3.3</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>4.0</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>4.8</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>5.4</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>5.6</td>
<td>30</td>
</tr>
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<td></td>
<td>7.0</td>
<td>5.2</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>5.8</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>6.3</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>12.0</td>
<td>8.5</td>
<td>260</td>
</tr>
<tr>
<td>BTAC</td>
<td>3.6</td>
<td>4.2</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>5.4</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>10.4</td>
<td>6.3</td>
<td>17</td>
</tr>
</tbody>
</table>

* BDDAC or BTAC solutions (50 ppm, 25 mL) were photodegraded with 50 mg of TiO₂ 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 photodegradation.

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. TiO₂ has an amphoteric property with the isoelectric point (pI) of 5.3, to which the pH value during photolysis gradually approaches.

Since the TiO₂ surface in an acidic medium possesses positively charged -O²⁻ groups, the cationic BDDAC is repelled and therefore the decomposition is slowed. On the other hand, the TiO₂ surface is negatively charged in an alkaline medium due to the presence of -O²⁻. The BDDAC surfactant cations must be strongly adsorbed on the negative TiO₂ surface by coulombic interaction. Hence the attack of more reactive ‘OH radical, formed via the formation of electron-hole, to the aromatic group is lowered. Consequently, the catalytic action of TiO₂ is weakened in an alkaline medium.

![Fig.-3](image-url)

**Fig.-3** Effect of the amount of TiO₂ catalysis on the photodegradation rate of BDDAC.

The effect of the amount of TiO₂ 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 TiO₂ 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% D₂O 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:<br>Light absorption by TiO₂ created electron/hole pairs. The holes are subsequently trapped by surface hydroxyl groups yielding adsorbed 'OH radicals. Alternatively, direct hole scavenging by the aromatic group in BDDAC adsorbed on the TiO₂ surface could occur. These '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 TiO₂ aqueous suspensions. The surface activity was lowered by ultraviolet irradiation. The long alkyl chain and the aromatic moiety in the surfactants were competitively decomposed.

Acknowledgments

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