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Photodegradation of surfactants with TiO_2 semiconductor for the environmental wastewater treatment

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Abstract. Surfactants were photodegraded in TiO_2 suspensions under UV irradiation. The photodegradation mechanism of chemical structures of surfactants, the time scale in the photooxidative decomposition and the intermediate products were investigated. Various surfactants are widely used in domestic and industrial fields. However, they are not easily biodegraded through bacteria and are accumulated in the nature of alkylphenylpolyoxyethylene which generates toxic intermediates of alkylphenol derivatives which are immiscible in water during biodegradation. Since the cationic surfactant exhibits antimicrobial activity, the biodegradation is poor. The other strategy of this study is also a harvest of photocurrent during the transformation process.

Keywords. Surfactants; photodegradation; TiO_2 electrode assembly; oxyethylene group.

1. Introduction

The photooxidation of organic substances catalyzed with TiO_2 semiconductor was first published by Carry in 1976 who dealt with the photodecomposition of chlorobiphenyl compound in heterogeneous TiO_2 particle dispersion. The fundamental and applied researches for the environmental wastewater treatment have been actively advanced globally to solve severe aquatic and air contamination. In particular, the photodegradation of carcinogenic chloroorganics of trichloroethylene, chlorophenol etc., phosphorus-, nitrogen- or sulphur-containing agrochemicals such as pesticides and herbicides, cyanide compounds and polymers of polyvinylalcohol, polyethyleneglycol etc. has been extensively reported by many researchers.

The photocatalytic degradation with TiO_2 catalyst is one of the most promising procedures. All kinds of surfactants can be mineralized to CO_2, H_2O and other inorganic ions and organic acids in a short time without formation of toxic intermediates, irrespective of the structures of surfactants. Since an amphiphilic surfactant contains both hydrophobic alkyl group and hydrophilic functional group in one molecule, the details of decomposition mechanisms and adsorption behaviours on the surface can be informed at a molecular level.

In this paper, we describe the recent experiment on the photomineralization or phototransformation for functional moieties of sulphate, phosphate and quaternary ammonium group and hydrocarbons of an alkyl chain and an ethoxyl group in TiO_2 dispersion systems. Further, the TiO_2-fixation procedure on glass fibres, glass beads, ceramic tiles and honeycombs is studied from the viewpoint of an industrial application for continuous and large scale treatments. The fixation procedures need no operation

for removal. The photooxidative activity still maintains even in repeated runs(turn-over). The electrochemical decomposition of organic pollutants containing surfactants such as the big TiO_2 semiconductor of TCO (transparent conductive oxide) electrode assemblies has been carried out by us [1]. The other strategy of this study is also a harvest of photocurrent during the transformation process. We introduce the recent results later in section 7.

2. Photodegradation principle of organics catalyzed by TiO_2 semiconductor

The photochemical and physical kinetics on photoexcitation processes in semiconductor TiO_2 particles are shown in figure 1.

TiO_2 is a *n*-type semiconductor having a bandgap of 3·2 eV. Therefore, the charge separation by UV illumination below 387 nm occurs to generate electron holes (h^+) in a valence band and electrons in a conduction band respectively (1). The holes capture the electrons from H_2O molecules adsorbed and/or hydroxyl groups bound on the TiO_2 particle surface (2 and 3). Concomitantly, the dissolved oxygen accepts the electron from the conduction band to form $\cdot O_2^-$. This radical reacts with protons in aqueous solution to generate ·OOH radicals (4 and 5). The highly reactive radicals were confirmed by spin-trapping ESR measurements using DMPO reagent.

$$TiO_2 + h\nu \rightarrow TiO_2\{e^- \cdots h^+\} \rightarrow e^- CB + h^+ VB \quad (1)$$

$$\{OH\text{-}\}\ \text{bound} + h^+ VB \rightarrow \{\cdot OH\}_{\text{bound}} \quad (2)$$

$$\{H_2O\}\text{ads} + h^+ VB \rightarrow \{\cdot OH\}_{\text{ads}} + H^+ \quad (3)$$

$$\{O_2\}\text{ads} + e^- CB \rightarrow \{\cdot O_2^-\}_{\text{ads}} \quad (4)$$

$$\{\cdot O_2^-\}_{\text{ads}} + H^+ \rightarrow \{\cdot OOH\}_{\text{ads}}. \quad (5)$$

The actively oxidative radicals of ·OH or ·OOH are attacked to the organics adsorbed or assessed on TiO_2 surface and the organics are photooxidized. The direct oxidation of

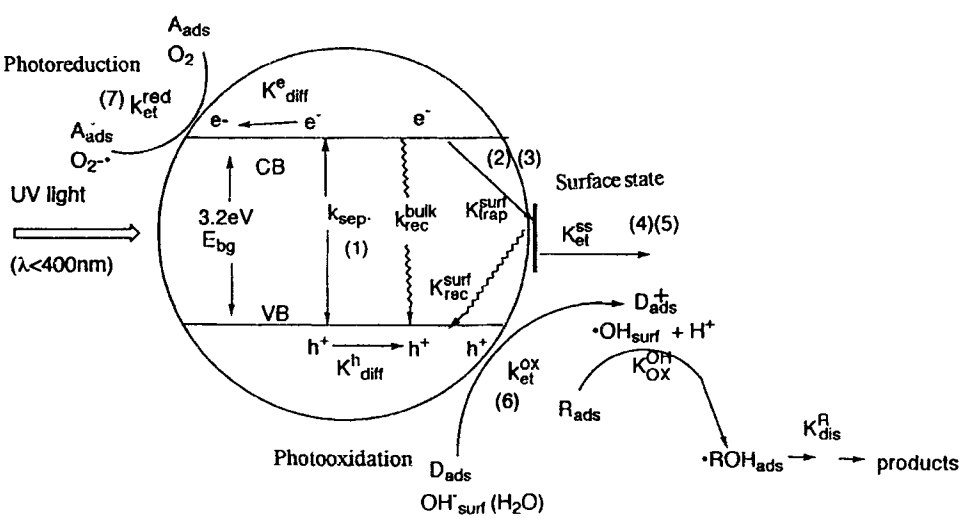

Figure 1. The photophysical and photochemical processes in a semiconductor.

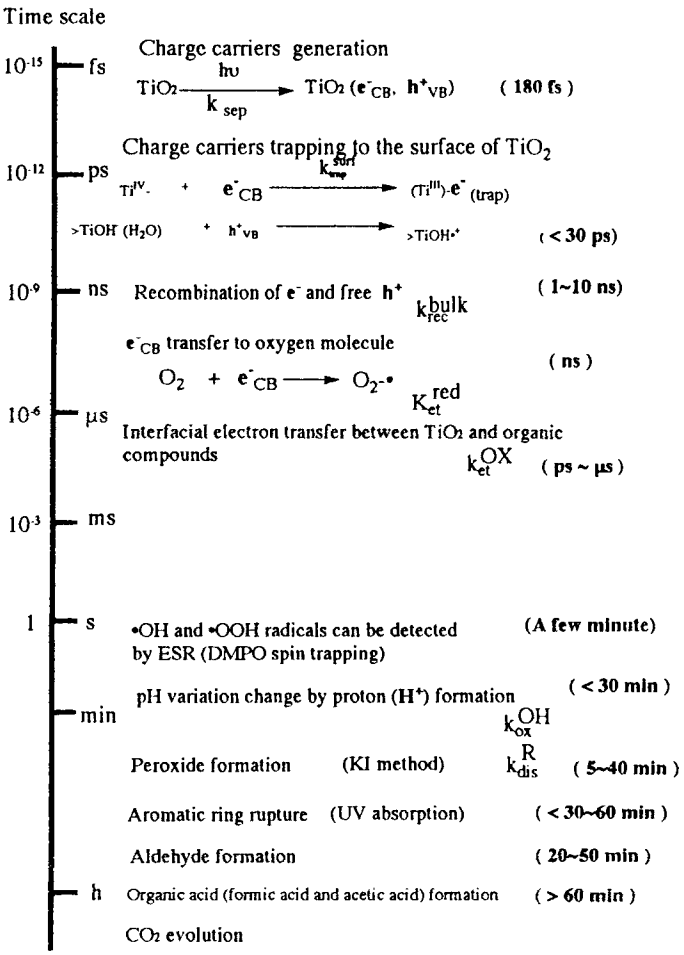

Figure 2. Time scale of photocatalytic oxidation.

the organics with the holes in the valence band takes place in a parallel manner. Particularly, the π-electrons in an aromatic ring capture the electrons by the hole to form cationic radicals.

3. Time scale in the photooxidative decomposition

The mechanistic details on the charge separation rate in semiconductor particles and electron transfer rate have been studied by laser flash photolysis. The time scale on the photooxidative degradation process for an organic substance is summarized in figure 2.

When TiO_2 particles are irradiated by ultraviolet (UV) light, electrons and holes are formed within an ultrafast rate below 180 fs in a crystal, followed by capturing the electrons at the defecting moiety in a lattice on TiO_2 surface. The electron holes react with the hydroxyl groups (and/or bound water) combined with TiO_2 surface at the rate within 30 ps. The transfer rate of electrons in a conduction band to O_2 molecules is relatively slow in nanosecond order as Gerisher *et al* has postulated [2].

This step is a rate-determining step in a photocatalytic reaction. Consequently, no photodecomposition proceeds effectively in the absence of oxygen molecules. Many charge-carriers (e^- and h^+) formed by photoexcitation within $1 \sim 10$ ns disappear by the recombination of e^- and h^+ in a TiO_2 bulk and then the electron transfer occurs between an organic compound and TiO_2 particles.

Although the rate is dependent on the kind of an organic compound, this process proceeds within ps to ms. Formation of ·OH or ·OOH radicals is detected within 30 min and simultaneously protons are generated by photolysis of H_2O. Totally, the reaction solution becomes acidic. The hydrocarbon moiety in a surfactant is attacked

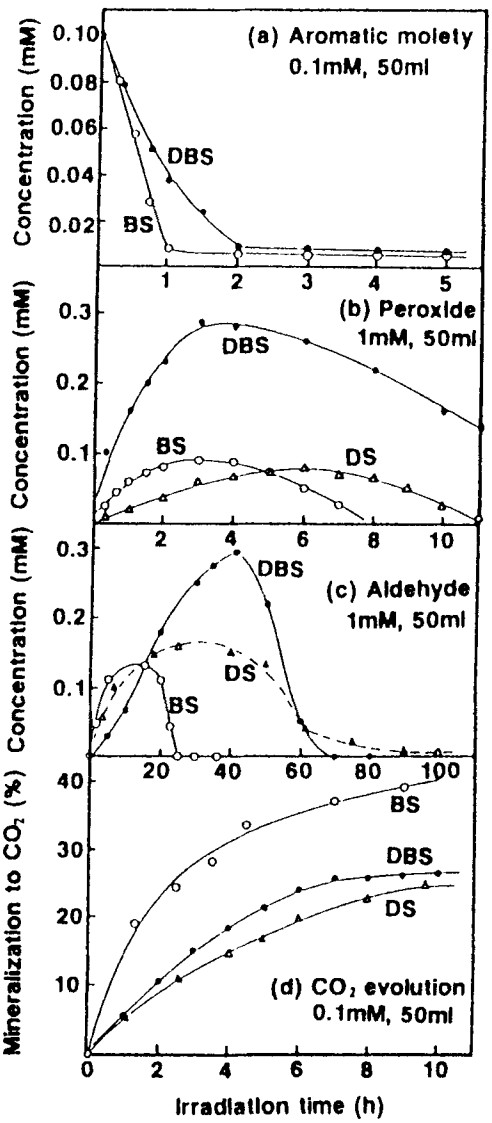

Figure 3. Photodegradation of anionic DBS and its reference substances DS and BS in air-equilibrated aqueous suspension (50 ml, 1 or 0·1 mM) of TiO_2 (100 mg) under Hg-lamp irradiation.

by actively oxidative species to prepare a hydroxylated compound and a hydroxyperoxide derivative (confirmed by the KI method). Subsequently, these compounds are mineralized to CO_2 via aldehyde or carboxylic acid intermediates by photooxidation and/or autooxidation. A hetero atom moiety is photoconverted to inorganic ions. An aromatic moiety such as benzene$^-$ or pyridine$^-$ ring is easily cleaved. Formation of peroxide, the ring-opening of benzene group, formation of aldehyde and CO_2 evolution in the photodegradation of DBS (sodium dodecylbenzene sulphonate) are shown in figure 3.

The time required for secondary oxidation on TiO_2 surface or in a bulk solution occurs in the order of several minutes to hours.

4. Adsorption and photodecomposition rate

The photodegradation rate in heterogeneous TiO_2 dispersion follows Langmuir–Hinshelwood equation (L–H plot) using a monomolecular layer reaction on a solid catalyst.

$$r_{\text{initial}} = kK/(1 + KC) \tag{6}$$

$$1/r = 1/kK \times 1/c + 1/k, \tag{7}$$

where k is a reaction kinetic constant, K an adsorption equilibrium constant, and C an initial concentration. The plot of the reciprocal kinetic constant against the reciprocal concentration exhibits a linear relationship. The intercept is k^{-1} and the slope is kK^{-1}. The decomposition reaction of a surfactant is very complicated because of many competitive reactions. Therefore, the definiton of an apparent reaction rate constant k is difficult.

Figure 4 shows the L–H plot for the photodecomposition of anionic DBS and cationic BTDAC (benzyltetradecyl dimethyl ammonium chloride). The adsorption

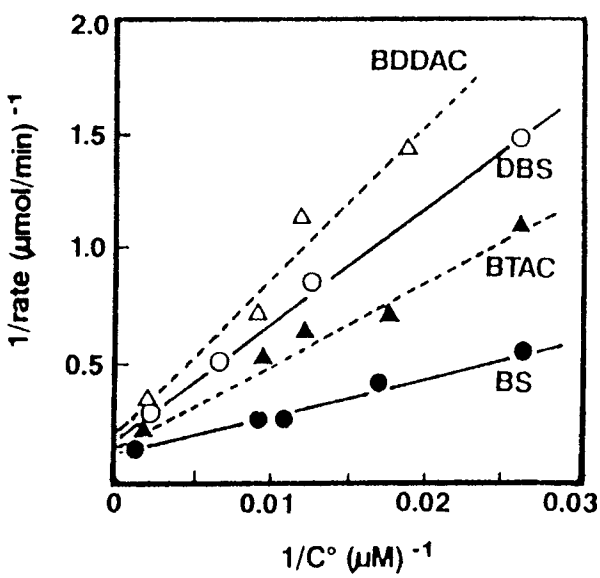

Figure 4. Langmuir–Hinshelwood plot of reciprocal initial rate against reciprocal initial concentration for DBS, BDDAC, BS, and BTAC.

equilibrium constant calculated from the plot is determined to be almost 5·9 mM ± 0·03 mM/min. On the other hand, the rate constant is dependent on the chemical structure of a substrate. The lifetime of ·OH or ·OOH radicals generated on TiO_2 surface is short that the adsorption of a substrate on TiO_2 surface is remarkably affected on the decomposition rate. TiO_2 has an amphoteric compound having the isoelectric point $pH_{pzc} = 6·2$. The surface potential is a positive charge in acidic range, while it is a negative charge in alkaline range. Under UV irradiation, the degraded solution become acidic according to (3) in section 2 and the TiO_2 surface is charged positively. Therefore, an anionic surfactant is adsorbed electrostatically on TiO_2 surface and the photodegradation rate is accelerated. On the other hand, that of a cationic surfactant is slower because of electrostatic repulsion.

5. Experimental procedures (photodegradation in a heterogeneous dispersion)

In a batch system, a surfactant solution (50 ml) with anatase TiO_2 particles (100 mg Degussa P-25, average particle size 30 nm) was placed in 70 ml reaction vessel and was illuminated with a mercury lamp ($\lambda > 330$ nm, Toshiba SHL-1002A, 75 W) and stirred magnetically. After illumination, the degraded solution was centrifuged and filtered with a millipore filter (0·22 μm) to remove TiO_2 particles.

6. Degradation mechanism for the chemical structures of surfactants

6.1 *Nitrogen-containing surfactants*

There are few papers on the photocatalytic oxidation of nitrogen-containing compounds. Although the photodecomposition for agrochemicals of a herbicide or a pesticide containing the structures of benzamide. pyridine, triazine were published, the photoconversion of a nitrogen moiety has received much attention. Matthews *et al* 1991 reported the photooxidation of various nitrogen-containing organics [3]. However, the relationship between the structure of nitrogen and the ratio of NH_4^+ ion/NO_3^- ion and the formation processes have not been revealed. The concomitant formation of NH_4^+ ion NO_3^- ion on nitrogen-containing substances in the photocatalytic oxidation processes is very interesting.

Among surfactants, most of them have cationic surfactant having strong antibacterial activity, a nonionic one and an amphoteric one having non-irritation to skin which contain quaternary ammonium nitrogen (–$\overset{|}{\underset{|}{N}}$–), secondary amine (–NH–), tertiary amine (>NH<) and peptide (–CONH–) in their chemical structures. We discuss the decomposition mechanism for the nitrogen moieties of the following surfactants [4]: cationic BTDAC and dodecyl pyridinium chloride (DPC), nonionic dodecanoyl-N-(2-hydroxyethyl) amide (N–DHA) and dodecanoyl-N,N-*bis*(2-hydroxyethyl) amide (N, N–DHA), amphoteric dodecyl-β-alanine (C_{12}-β-Ala), N-(2-hydroxydodecyl)-N-(2-hydroxyethyl)-β-alanine (C_{12}-HAA), N-dodecylamidopropyl,-N,N-dimethylammonium acetate (C_{12}-amidobetaine) as shown in figure 5.

A surfactant solution (0·1 mM, 50 ml) was photodegraded according to the method as mentioned in section 5. The nitrogen moieties in a nitrogen-containing surfactant was photoconverted to NH_4^+ ion and NO_3^- ion, but not to inorganic compounds of N_2 and NO_2 gas.

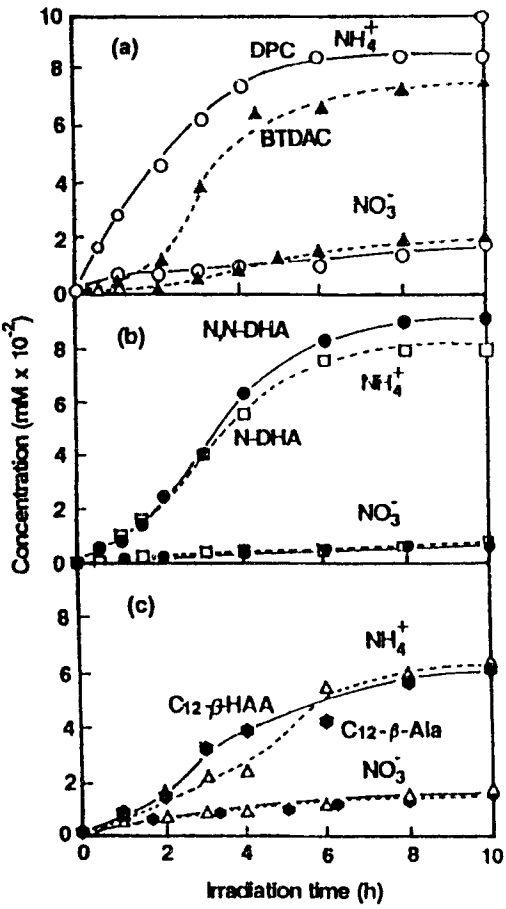

Figure 5. Formation of ammonium and nitrate ions in the photomineralization of (a) ○, DPC and ▲, BTDAC; (b) □, N-DHA and ●, N,N,-DHA; (c) Δ, C_{12}-β-Ala and ★, C_{12}-β-HAA as a function of irradiation time.

NH_4^+ ion was mainly formed in comparison with the formation ratio of NH_4^+/NO_3^-. The formation rate is dependent on the chemical structure. On the other hand, the amount of NO_3^- ion was almost 0·01 mM after irradiation of 8 h irrespective of the chemical structure. The decomposition of DPC easily caused the ring-opening of pyridine moiety which was confirmed by UV spectroscopy. The rate of NH_4^+ ion formation is very fast. The decomposition rate of amphoteric surfactants is slower than that of cationic and nonionic surfactants. Since an amphoteric one has both negative and positive charges it is the reason attributed to the unstable adsorption on TiO_2 surface. The identification of the intermediates in the photodegradation of amphoteric C_{12}-amidobetaine was done by GC-MS and NMR techniques. The C–N bond in C_{12}-amidobetaine was cleaved as an initial step. The intermediates of dodecanoamide, tertiary amine and/or quaternary ammonium were produced subsequently. The intermediate of amide is easily hydrolyzed to form NH_4^+ ions. By contrast, the intermediates of tertiary amine or quaternary ammonium were attacked by ·OH and/or ·OOH radicals to convert finally to NH_4^+ and NO_3^- ions. The decomposition of nitrogen

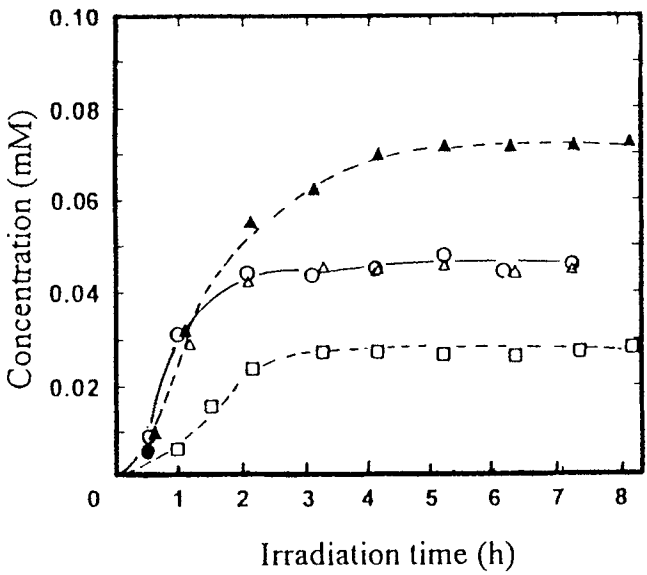

Figure 6. SO_4^{2-} ion formation from the degradation of DBS; ○, BS; Δ, SDS; ▲, and TPA; □, in the presence of TiO_2 catalyst.

moieties in surfactants is slower in the following order: pyridine ring > secondary amine > tertiary amine > peptide > quaternary ammonium.

To reveal the formation mechanism of NH_4^+ and NO_3^- ions, various model compounds of alkylamide and hydroxy succinoimide were photodegraded. The relationship between formation ratio of NH_4^+/NO_3^- and chemical structure was also investigated. When the photodegraded intermediate is a primary amine or an amide, NH_4^+ ion is preferentially produced. On the other hand, when the nitrogen atom in an organic compound is attacked by ·OH and/or ·OOH radicals to form a hydroxylamine derivative, NO_3^- ions is predominantly produced [5].

6.2 *Sulphur-containing surfactants*

The sulphonate ($-SO_3Na$) in anionic DBS, the sulphonate ($-OSO_3Na$) in sodium dodecyl sulphate and the thiocarboxylic salt in TPA (S-dodecylthioproprionic acid salt) can be photomineralized to SO_4^{2-} ion via SO_3^- ion, but not to form H_2S or HS^- derivative. Even if S^{2-} ion can be formed, it will change to SO_4^{2-} ion immediately by photooxidation [6]. The sulphonate group connected to a benzene ring like DBS can be easily converted to SO_4^{2-} ion as shown in figure 6.

Comparing DBS with BS, the formation rate of SO_4^{2-} is the same and is not dependent on the alkyl chain length. The hydrophilic sulphonate is adsorbed on TiO_2 surface more selectively than the hydrophobic alkyl chain. The initial formation rate of SO_4^{2-} ion from the decomposition of TPA was relatively slow compared to that of DBS and SDS. With respect to TPA, the decomposition proceeds from the terminal carboxyl group in TPA. The fission of C–S bond and the attack of ·OH and OOH radicals then occur. A polymer such as polystyrene sulphonate can be easily desulphonated.

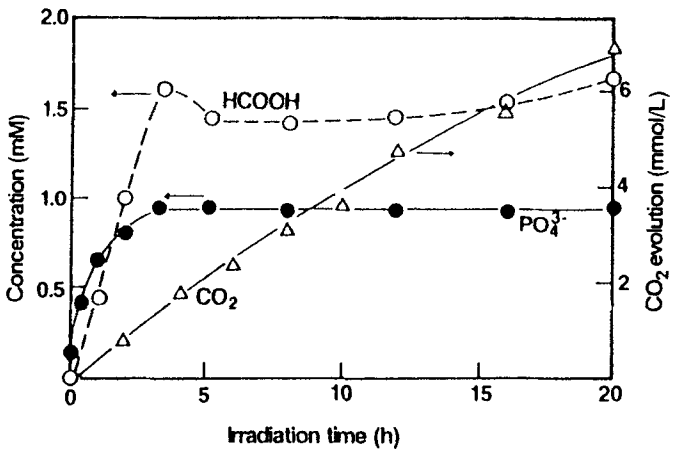

Figure 7. Photodegradation of $C_{12}E_2P$ in the presence of TiO_2 catalyst.

6.3 *Phosphor-containing surfactants*

The phosphorous organics employed as agrochemicals are either strongly toxic or carcinogenic. There are few reports on the photodecomposition of phosphor-containing materials. Figure 7 shows the degradation of dodecyl*bis*(oxyethylene) phosphate (C_{12}-EP). The phosphate group is photomineralized very quickly. In an initial photoillumination, it can be converted to PO_4^{3-} ion [7].

6.4 *Surfactants composed of hydrocarbon*

The photodecomposition of a surfactant composed of a long alkyl chain or an ethoxy group gives oxidative intermediates such as peroxides, aldehydes and short carboxylic acid and finally CO_2 gas is evolved. A nonionic surfactant having a different alkyl chain and oxyethylene group is photodegraded as shown in figures 8(a) and (b). The ethoxyl group is degraded more rapidly than the alkyl group. Preferential CO_2 evolution is carried out in an initial degradation process. An amount of CO_2 gas from the degradation of $C_{12}E_m$ ($m = 5$, 6, 7 and 8) homologues (1 mmol) is closely related to the number of ethoxyl groups after irradiation of 8 h (see figure 8(a)). Namely, about 10, 12, 14 and 16 mmol of CO_2 is evolved from $C_{12}E_m$. The degradation of C_nE_8 ($n = 10$, 12, 14, 16 and 18) gives the same amount of CO_2 irrespective of alkyl chain length as shown in figure 8(b). As a result, the oxyethylene group is degraded more easily than the aklyl group and each oxyethylene group is cleaved, one by one, from the terminal [8].

In order to examine the decomposition of alkyl chain, NMR spectral pattern for the degraded D_2O solution of sodium dodecanoate (10 mM/D_2O) is illustrated in figure 9.

The terminal methyl proton at 1·14 ppm and the α-methylene proton at 2·06 ppm are absorbed even after long irradiation time. On the other hand, the signal of alkyl chain at 1·18 ppm decreases when the irradiation time is increased. From the integration of the alkyl chain signal, the dodecyl moiety decreases one methylene group after 2 h-irradiation. Subsequently, the alkyl chain length decreases with irradiation time. The number of ethylene group is four after 10 h-irradiation. The alkyl chain is gradually

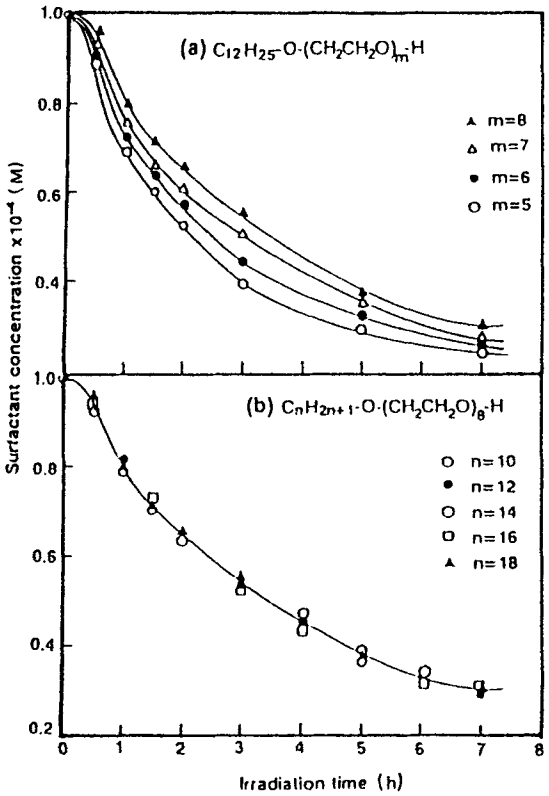

Figure 8. Temporal photodecomposition of (a) $C_{12}E_m$ ($m = 5$, 6, 7 and 8) and (b) C_nE_g ($n = 10$, 12, 14, 16 and 18) surfactant solutions (0·1 mM, 50 ml) with TiO_2 (100 mg) monitored by the extraction method

decamped from the terminal position in this way. After irradiation of 30 min, the peak belonging to formyl proton (assigned to aldehyde) is absorbed at a low magnetic field of 8·37 ppm. Further, the signal (1·99 ppm) attributable to acetic acid increases with irradiation time.

7. Photoelectrochemical decomposition of surfactants on a TiO_2/TCO electrode assembly

Promotion of charge separation following irradiation and minimization of electron/hole recombination can occur in a semiconductor film electrode in which TiO_2 particulates are fixed on a transparent conductive oxide (TCO) glass plate. Since the electrons generated by photoexcitation in TiO_2 particles flow to the outlet circuit through a TCO layer, the charge separation is promoted in TiO_2 particles and the recombination is depressed. The colloidal TiO_2 membrane on an electrode surface is so porous that the interesting photochemical and photoelectrochemical characteristics are examined. Recently, the photodecomposition of chloroorganics [9], dyes [10] and surfactants [11] was carried out. TiO_2 powders (Degussa P-25, anatase) dispersed in aqueous solution were loaded onto a TCO glass plate (Asahi Glass Co. Ltd. transparent

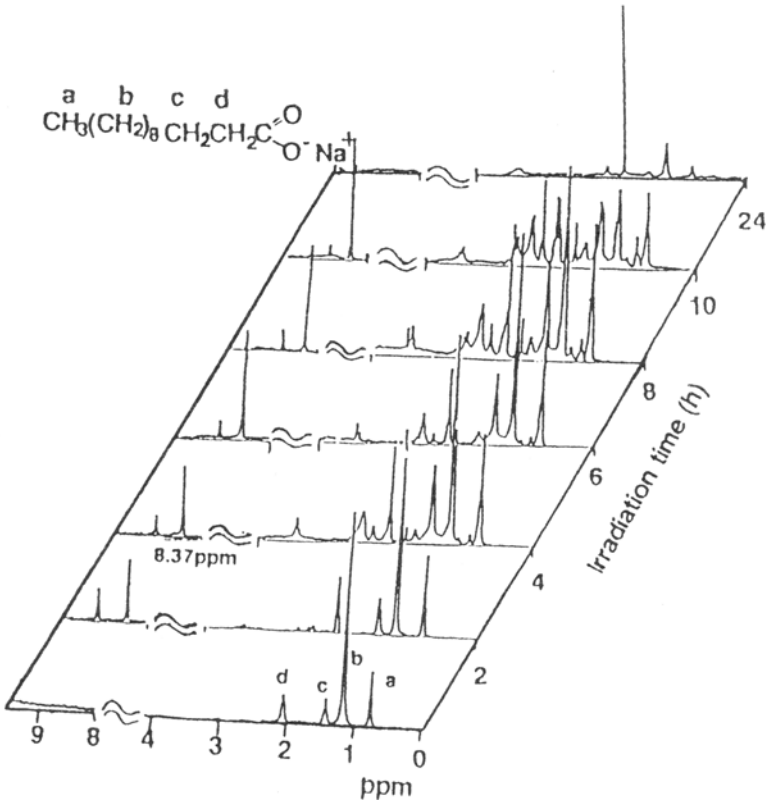

Figure 9. Temporal NMR spectral profiles in the photooxidative decomposition of sodium dodecanoate in D_2O solution (10 mM).

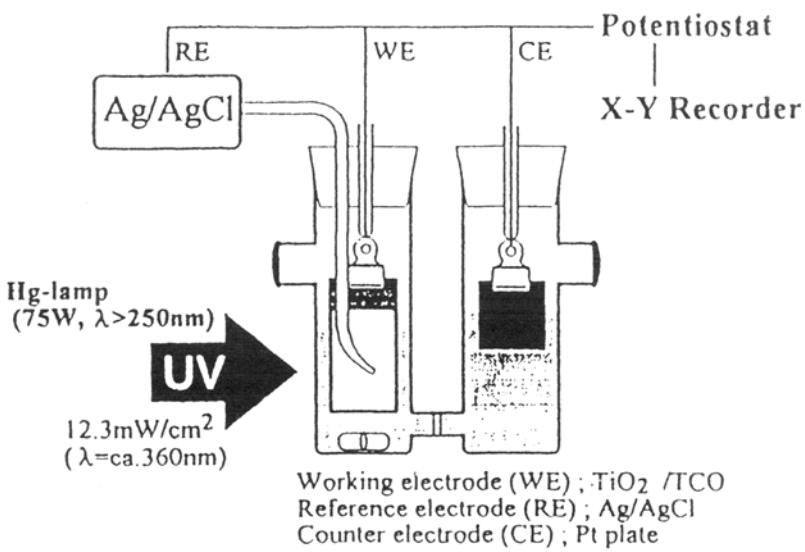

Figure 10. Photoreaction cell assembly for potentiometric and voltage-static electrolysis

conductive oxide coated glass plate of fluorine-doped SnO_2) and subsequently dried in air. The plate was sintered for 2 h at 300°C in a furnace to prepare a particulate film electrode. The TCO coating was 2·1 μm thick, whereas the thickness of the TiO_2 thin film was 4·2 μm. The quantity of TiO_2 on the area of $20 \times 30\,mm^2$ was about 5 mg. The DBS solution (0·1 mM, 50 ml) was contained in a Pyrex glass photoreactor. The anode electrode was a TiO_2/TCO plate and the counter electrode (the cathode) was a Pt plate ($20 \times 20\,mm^2$); the reference electrode was a Ag/AgCl electrode connected to the assembly via a salt as shown in figure 10.

The photodegradation of a DBS solution at constant applied voltage (5 V) is illustrated in figure 11(a). Addition of supporting electrolytes such as Na_2SO_4 or NaCl (0·1 M) enhances somewhat the photodegradation of the surfactant in comparison with that carried out in an electrolyte-free system. We have reported extensively in earlier reports that the active oxidizing species in photooxidation is the ·OH radical. The CO_3^{2-} ion is a well known ·OH scavenger and the photooxidation of DBS is therefore expected and is observed to be much slower in carbonate media.

The TiO_2 electrode potential in the presence of electrolytes stays anodic. As a result, the redox activity of photogenerated electrons and holes should be accelerated. Consequently, the active oxygen species (e.g., ·OH, ·OOH, and/or $\cdot O_2^-$-radicals) that are likely to oxidize DBS are probably generated in greater quantity. Insofar as the photodegradation of DBS in the presence of Na_2CO_3 is concerned, the increase in [HO·] from the hydrolysis of the carbonate ion increases the solution *p*H and consequently renders the TiO_2 particulate surface negatively charged (the isoelectric point of TiO_2 is less than *p*H 6). Under these conditions, adsorption of negatively charged DBS molecules onto the photocatalyst surface is minimized, if not suppressed, and photodegradations should be retarded even further, relative to other electrolytes.

The maximal rate (determined from HPLC experiments having a UV detector), $k = 2{\cdot}3 \times 10^{-2}\,min^{-1}$, for the photodegradation of DBS is exhibited at an applied potential of +0·3 V. At this applied bias, the photocurrent reached a maximal value immediately after photoreaction and gradually decreased to a constant value (plateau at $\approx 50\,\mu A$) at 2 h of irradiation time (figure 11(b)). We attribute the maximal photocurrent to the oxidation of formic acid which was the principal intermediate product before CO_2 evolution. Electrons that appear in the conduction band of TiO_2 and lead to increased photocurrent, originate from reactions 8 and 9

$$HCOOH + h^+ \rightarrow HCOO\cdot + H^+ \tag{8}$$

$$HCOO\cdot + TiO_2 \rightarrow CO_2 + H^+ + TiO_2(e_{CB}^-). \tag{9}$$

The photocurrent flows through the external circuit. The "current doubling" phenomenon reported by others evidently also takes place in the photooxidation process of the DBS surfactant.

The behaviour of the photogenerated current as a function of irradiation time at a bias of −0·3 V fluctuates between anionic and cationic levels. The current was rather small compared with that at other applied potential bias. This potential of −0·3 V refers to the zero current potential and corresponds approximately to the flat band potential of the conduction band of TiO_2 under the prevailing conditions. The stagnant electrons in the bulk of TiO_2 are deactivated by recombination with the valence band holes. Thus, the reactivity was lower and formation of active oxygen species was suppressed leading to a decrease in the rate of degradation of DBS. At a −0·5 V bias,

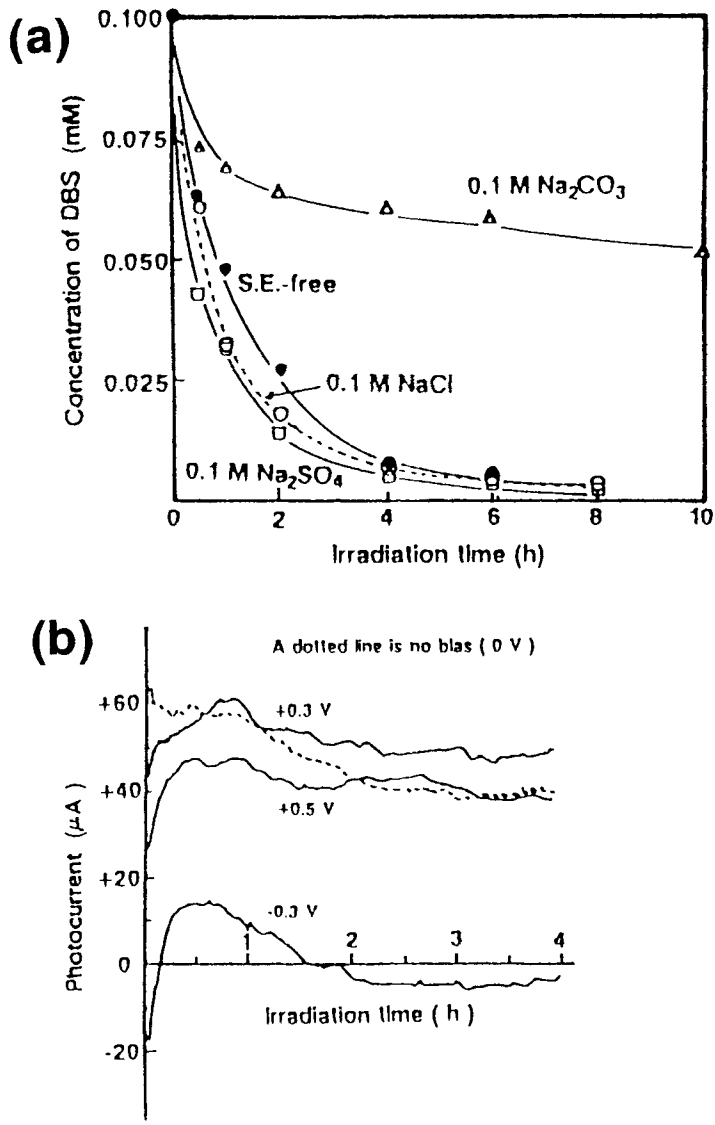

Figure 11. (a) Temporal changes in the concentration of DBS (0·1 mM) in a photoelectrochemical TiO_2/TCO cell assembly in various electrolyte (0·1 M) systems at a constant bias of 5 V. S.E. stands for a supporting electrolyte.
(b) Photocurrent generated in a TiO_2/TCO electrode assembly during the photodegradation of DBS by a potentiostatic electrolysis.

any accumulation of electrons at the TiO_2/solution interface enhances the reduction of O_2 and/or H^+, such that the largest quantity of electricity (in terms of number of coulombs) based on a cathodic current was measured at this bias. On the other hand, the holes formed by charge separation are diffused to the bulk of TiO_2 particulates and formation of ·HO radicals is thereby limited. Consequently, the rate of photodegradation of DBS decreased.

Applied voltages were from a DC potentiostat and the UV illumination was provided by a Toshiba mercury lamp. The potentials at the TiO_2 electrode were measured with an electrometer. The temporal changes in the concentrations of the photodegraded DBS surfactant were monitored by high performance liquid chromatography (HPLC) using UV-detection. Figure 10 illustrates the photoelectrolysis setups for potentiometric and photocurrent measurements, respectively. The latter measurements were carried out using a potential step method with a potentiogalvanostat. The temporal dissappearance of DBS was also undertaken electrolytically using a pair of Pt electrodes (as anode and cathode).

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