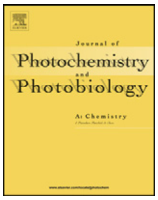
Journal of Photochemistry and Photobiology A: Chemistry 229 (2012) 53–59

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Surfactant effect on titanium dioxide photosensitized oxidation of 4-dodecyloxybenzyl alcohol

Marta Bettoni[a], Lucia Brinchi[b], Tiziana Del Giacco[b], Raimondo Germani[b],*, Sara Meniconi[a], Cesare Rol[b], Giovanni Vittorio Sebastiani[a],**

[a] Dipartimento di Ingegneria Civile ed Ambientale, Università di Perugia, Via G. Duranti, 06125 Perugia, Italy
[b] CEMIN, Centro di Eccellenza Materiali Innovativi Nanostrutturati, Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

ARTICLE INFO

Article history:
Received 21 September 2011
Received in revised form 5 December 2011
Accepted 10 December 2011
Available online 21 December 2011

Keywords:
Titanium dioxide
Surfactants
Micelles
Oxidation
Photocatalysis

ABSTRACT

The TiO_2 photosensitized oxidation of 4-dodecyloxybenzyl alcohol (**1**), water insoluble, was investigated in aqueous surfactant solutions. A variety of surfactants of different charge type was used and in some cases the pH effect was investigated. The considered surfactants are: cationic (cetyltrimethylammonium with various counterions, CTAX with X = Cl, Br and OMs), zwitterionic (dimethyldodecylamine oxide, DDAO, tetradecyltrimethylammonium propane sulfonate, SB3-14, and tetradecyltripropylammonium propane sulfonate, SBPr3-14) and anionic (sodium dodecylsulfate, SDS, sodium dodecylbenzenesulfonate, SDBS). The reaction, that is practically absent in water, is greatly enhanced by several surfactants at concentrations higher than cmc and the effect is strongly dependent on the nature of the surfactant. A rationale for that is suggested, with micellar aggregates rather than monomeric surfactants playing a main role. The effects of surfactant concentration on the conversion to the corresponding benzaldehyde were studied. We suggest that the increase of the surfactant concentration leads to an increase of the number of substrate molecules, solubilized (through co-micellization) in micelles, which can be transported close to the TiO_2 particle surface where they react. After a certain concentration which varies with the nature of the surfactant, the presence of the competitive partition between the co-micellized substrate **1** adsorbed on TiO_2 (where reaction occurs) and the co-micellized substrate in the bulk tends to limit more and more the beneficial kinetic effect of the surfactant. The surfactant that gives in water the best performance in terms of 4-dodecyloxybenzaldehyde yield (42%) is SB3-14 0.015 M. Moreover, a better yield (55%) is obtained in the presence of surfactant CTABr 0.05 M with added HCl 0.1 M.

1. Introduction

The TiO_2 photosensitized oxidation in water of organic materials, as pollutant models, has been extensively studied and reviewed [1]. In this context the role of surfactants in the process is an environmentally interesting topic and has been generally investigated considering their degradability in the reaction medium [2–4] or their kinetic effect on the photodegradation of totally or partially soluble compounds [5–7]. Concerning the last point, it has been observed that the effect (beneficial or not) is dependent both on the substrate and on the surfactant structure. Few studies have been reported on the effect of surfactant structure and concentration on the rate of this photochemical process considering insoluble (and consequently non reactive in the absence of surfactants) substrates [8].

In this paper we report on the TiO_2 photosensitized oxidation of a water insoluble organic substrate in aqueous surfactant solutions, using a variety of surfactants, both commercially available and not. We introduced also some modifications in the structure of the surfactant, in order to understand the possible role played by the surfactant type on the photocatalytic activity of TiO_2.

In particular, we used cationic, zwitterionic (sulfobetaines and amine oxides) and anionic surfactants shown in Scheme 1, where acronyms used are also indicated. In the cationic family the counterion was changed, in the sulfobetaine family the head group bulk was increased and in the anionic family the nature of the negatively charged group was changed. In all systems the concentration effects were investigated and in some cases the pH was changed. As a model reaction we chose the photocatalytic oxidation of two *p*-alkoxybenzyl alcohols to the corresponding aldehydes and focused our attention on the amount of aldehyde produced; the reaction is shown in Scheme 2. This is an oxidative transformation of

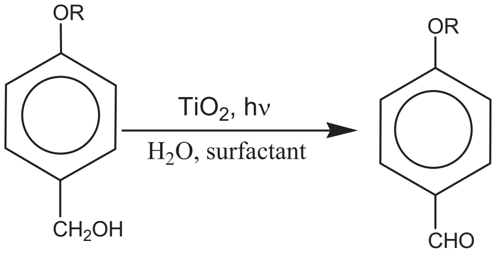
---

* Corresponding author. Tel.: +39 075 5855632; fax: +39 075 5855560.
** Corresponding author at: Dipartimento di Ingegneria Civile ed Ambientale, Facoltà di Ingegneria, Università di Perugia, Via G. Duranti 93, 06125 Perugia, Italy. Tel.: +39 075 5853859; fax: +39 075 5853864.
E-mail addresses: germani@unipg.it (R. Germani), gseb@tech.ing.unipg.it (G.V. Sebastiani).

1010-6030/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2011.12.003

$CH_3(CH_2)_{14}CH_2N^+(CH_3)_3\ X^-$	CTABr (X = Br) CTACl (X = Cl) CTAOMs (X = OSO_2CH_3)
$CH_3(CH_2)_{10}CH_2N^+(CH_3)_2O^-$	DDAO
$CH_3(CH_2)_{12}CH_2N^+(R)_2(CH_2)_3SO_3^-$	SB3-14 (R = Me) SBPr3-14 (R = n-Pr)
$CH_3(CH_2)_{10}CH_2OSO_3^-\ Na^+$	SDS
$CH_3(CH_2)_{10}CH_2ArSO_3^-\ Na^+$	SDBS

Scheme 1. Surfactants used in this work with acronyms.



1: R= $CH_2(CH_2)_{10}CH_3$
2: R= CH_3

Scheme 2. Photo-oxidation reaction.

functional groups and this kind of reaction is fundamental in organic chemistry being often used in synthesis and also in manufacturing bulk chemicals [9–11]. In particular, as substrate we have considered 4-dodecyloxybenzyl alcohol (**1**), a completely water insoluble compound, initially comparing the obtained results with those observed with 4-methoxybenzyl alcohol (**2**). The last one is a more hydrophilic substrate, soluble in water, whose photocatalytic reaction has been extensively studied in acetonitrile [12] and in water [13], and its mechanism, operative in both media, is well understood. It's reasonable to assume the same mechanistic behavior for **1** that differs from **2** only for R chain length.

2. Experimental

2.1. General remarks

Melting points are uncorrected and registered on a Büchi 510 instrument. ^1H NMR spectra were measured on a 200 MHz FT Bruker instrument in $CDCl_3$ and chemical shifts are relative to internal TMS.

2.2. Material

Preparation and purification of surfactants has been described elsewhere [14,15]. CH_3CN (Carlo Erba, HPLC grade) and TiO_2 (P25, Degussa 99.5%, dried at 110 °C) were analytical grade commercial products. Internal standard, dibenzyl, was from Aldrich (99% pure) and used without further purification. Milli Q water (18 MΩ, pH 6.32) was used. 4-Methoxybenzylalcohol (**2**) was commercial sample, from Sigma–Aldrich, used without further purification.

4-Dodecyloxybenzylalcohol (**1**) was prepared from 4-hydroxybenzaldehyde. It was refluxed for 24 h in CH_3CN with dodecylbromide in the presence of K_2CO_3 and the resulting mixture was poured into water and diluted with Et_2O. The aqueous phase was separated and extracted twice with Et_2O; the combined organic extracts were washed twice with NaOH 10%, then with water until neutral pH; they were dried over Na_2SO_4 and evaporated in vacuum to give a pale yellow oil as crude product. The crude was crystallized from methanol at −20 °C to give a white crystalline solid, 4-dodecyloxybenzaldehyde, with m.p. < 30 °C [^1H NMR ($CDCl_3$, 200 MHz): δ 0.85–0.91 (t, CH_3); 1.10–1.50 (m, $8CH_2$); 1.55–1.90 (m, CH_2); 3.92–3.98 (t, CH_2); 6.95–7.15 (d, 2H); 7.75–7.95 (d, 2H); 10.00 (s, H)]. 4-Dodecyloxybenzaldehyde was reduced to the corresponding alcohol using $NaBH_4$ in a mixture of THF/CH_3OH (200 ml/3 ml). The mixture was initially heated to 50 °C and, after the reaction started, it was kept warm by the heat produced by the reaction. After 2 h the mixture was cooled in an ice-bath; after addition of H_2SO_4 10%, the mixture was poured into water and extracted three times with n-hexane. Combined organic extracts were washed with water until neutral pH and they were then dried over Na_2SO_4 and partially evaporated in vacuum. Resulting solution was kept at −20 °C and the white solid obtained was dried in vacuum overnight to give a crystalline solid, **1**, with m.p. = 68–70 °C [^1H NMR ($CDCl_3$, 200 MHz): δ 0.85–0.91 (t, CH_3); 1.10–1.50 (m, $8CH_2$); 1.55–1.90 (m, CH_2); 3.92–3.98 (t, CH_2); 4.61 (s, CH_2); 6.86–6.90 (d, 2H); 7.20–7.30 (d, 2H)].

2.3. Conductivity

Conductivity was measured with a conductimeter (Analytical Control, model 120) equipped with platinum cell (cell constant 1.13 cm^{-1}). Solutions were prepared in deionized bidistilled water at 25.0 ± 0.1 °C and kept under magnetic stirring during measurements. The values of the critical micellar concentration (cmc) and of the ionization degree (α) have been obtained by analyzing the experimental curves by Evans method [16].

2.4. Reaction of **1** in aqueous surfactant solutions

Reactions were carried out in 15 ml-cylindric flask equipped with cooled jacket and under magnetic stirring. Previously prepared surfactant solution (10 ml) was added to the substrate (0.05 mmol), the mixture was sonicated for ca. 5 min and thereafter stirred for 1 h at room temperature. TiO_2 P25 (17 mg) was then added and magnetically stirred for 1 h; the resulting heterogeneous mixture was then externally irradiated using a Helios Italquartz 500 W high pressure mercury lamp (through Pyrex filter) for 3 h. At the end of reaction a known amount of dibenzyl (internal standard) in ethyl ether and NaCl were added to the mixture. Extraction was carried out using Et_2O and few drops of MeOH. Due to difficult separation of aqueous and ethyl ether layers, centrifugation was necessary (10 min at 15,000 rpm) and ether was separated using Pasteur pipette. The aqueous layer was extracted 3 times. The combined organic extracts were dried over Na_2SO_4 and analyzed by GC.

2.5. Reaction in water

Reactions were carried out in 15 ml-cylindric flask equipped with cooled jacket and under magnetic stirring; 10 ml of water was added to the substrate (0.05 mmol) and the mixture was stirred for 1 h at room temperature. The mixture is homogeneous with substrate **2** and heterogeneous with substrate **1**. TiO_2 P25 (17 mg) was then added and magnetically stirred for 1 h. The resulting opalescent mixture was then externally irradiated using a Helios Italquartz 500 W high pressure mercury lamp (through Pyrex filter).

At the end of reaction, a known amount of dibenzyl was added as the internal standard in ethyl ether; in the case of substrate **1** NaCl was added to the mixture. Further elaboration was as described above.

2.6. Reaction in CH_3CN

Reactions were carried out in 15 ml-cylindric flask equipped with cooled jacket and under magnetic stirring; 10 ml of acetonitrile were added to the substrate (0.05 mmol) and the homogeneous mixture was stirred for 1 h at room temperature. TiO_2 P25 (17 mg) was then added and magnetically stirred for 1 h. The resulting opalescent mixture was then externally irradiated using a Helios Italquartz 500 W high pressure mercury lamp. At the end of reaction, a known amount of dibenzyl was added as the internal standard in ethyl ether and the mixture was poured into water. Elaboration was as described above.

2.7. Product analysis

Analysis of the reaction mixture was carried out quantitatively by GC on an HP 5890 instrument (FID) with on column injection, equipped with a 30 m × 0.53 mm DB5-MS J&W column, 1 μm film thickness. Response factors were determined by using known mixtures of the products and the internal standard dibenzyl. All analyses were made in duplicate and errors of <5% were obtained.

*2.8. Determination of substrate **1** solubility in surfactant solutions*

Substrate **1** was added to 50 ml of 0.05 M surfactant solution and the mixture was sonicated and stirred at 25.0 °C. Addition of substrates was continued until saturation. After centrifugation, a known aliquot (20 ml) of the limpid solution was withdrawn. After addition of dibenzyl as internal standard, further elaboration was as described for the reaction mixture work up (Section 2.4). Extracts were analyzed by GC.

3. Results

For the sake of comparison, preliminary experiments were carried out in water and in acetonitrile in the absence of surfactants; in Table 1 are shown the results of the photocatalytic oxidation of both substrates **1** and **2** in various reaction media. In acetonitrile the amount of aldehyde formed is smaller for substrate **1** than for substrate **2** (compare Entry 1 with Entry 6) and for the last one the yield is consistent with literature data [12a]. Substrate **2** is water soluble and its reaction takes also place in water, but yields are (nearly ten times) lower than in acetonitrile (compare Entry 6 with Entry 7). The pH plays a role in the product yield of reaction of this substrate and in particular the yield increases significantly at pH 1 (compare, for example, Entry 7 with Entry 10). On the other hand, the lack of solubility of substrate **1** in water can account for the absence (or almost) of product when the reaction medium is water (Entry 4). No improvement was registered for substrate **1** with a change of pH (Entry 5).

Table 1
Photocatalytic oxidation of 4-dodecyloxybenzyl alcohol (**1**) and 4-methoxybenzyl alcohol (**2**) in presence of TiO_2 in different reaction media.[a]

Entry	Substrate	Reaction medium	Reaction time (h)	4-alkoxybenzaldehyde (mol%)
1	**1**	CH_3CN	1	30
2	**1**	CH_3CN	2	47
3	**1**	CH_3CN	3	60
4	**1**	H_2O	3	1
5	**1**	H_2O–HCl 0.1 M	3	–
6	**2**	CH_3CN	1	75
7	**2**	H_2O	1	6
8	**2**	H_2O	2	10
9	**2**	H_2O	3	14
10	**2**	H_2O–HCl 0.1 M	1	31
11	**2**	H_2O–HCl 0.1 M	2	46
12	**2**	H_2O–HCl 0.1 M	3	82

[a] At room temperature; TiO_2, 17 mg; substrate, 0.05 mmol; yields by GC; the material recovery (unreacted alcohol + formed aldehyde) is quantitative (≥90%).

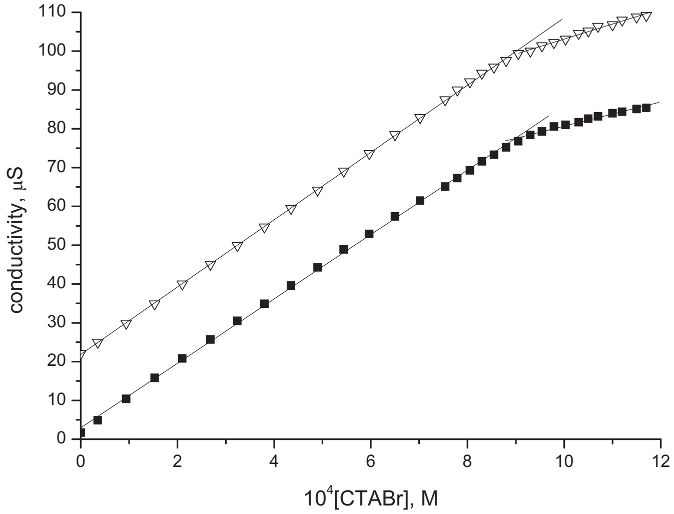


Fig. 1. Values of conductivity of suspension A (see Table 2) at different CTABr concentration with (▽) and without (■) TiO_2 added.

Conductivity experiments were carried out in the presence of surfactants and TiO_2 to understand if micelles are formed in the presence of the semiconductor in water and which is the influence of TiO_2 on the inset of micellization. Typical plots are reported in Fig. 1 for CTABr, with and without TiO_2. Values of the cmc are reported in Table 2 for all surfactants, both in the presence and the absence of TiO_2; zwitterionic surfactants cannot be studied with this method because of their neutral nature. Values of cmc in the absence of TiO_2 are consistent with literature data [17]. Data reported in Table 2 show that values of cmc are rather the same in the presence and in the absence of TiO_2. In the case of CTABr, cmc was measured in the presence of two different amounts of TiO_2 in water and values substantially do not vary.

Reaction of substrate **1** occurs in the presence of aqueous cationic surfactants CTACl, CTABr and CTAOMs, as shown in Table 3. The nature of the counterion in the cationic surfactant seems to play an important role: in fact the use of CTAOMs does not almost affect reaction and the yields are similar to those determined in water in the absence of any surfactant (compare Table 3 with Table 1). The effect of CTACl and CTABr was monitored at various surfactant concentrations and in both cases the behavior is similar, with

Table 2
Conductimetric values of cmc of surfactants used in absence and in presence of TiO_2.[a]

Surfactant	Water $10^3 \times$ cmc, M	TiO_2 aqueous system $10^3 \times$ cmc, M
CTACl	1.30	1.27
CTABr	0.898	0.886 0.871[b]
CTAOMs	1.41	1.50
SDS	8.27	9.27
DBSS	1.50	1.50

[a] Suspension A = TiO_2,70 mg, in 40 ml of water; measured pH of water is 6.35 and that of aqueous TiO_2 dispersion is 4.35.

[b] Suspension B = 500 μl of the suspension A in 100 ml of water.

Table 3
Photocatalytic oxidation of 4-dodecyloxybenzyl alcohol (**1**) in presence of TiO_2 in aqueous solutions of different cationic surfactants.[a]

Reaction medium	4-dodecyloxybenzaldehyde, (mol %)
CTACl 0.015 M	5
CTACl 0.035 M	11
CTACl 0.05 M	17
CTACl 0.065 M	18
CTACl 0.085 M	22
CTACl 0.1 M	18
CTAOMs 0.035 M	2
CTAOMs 0.05 M	1
CTAOMs 0.065 M	2
CTABr 0.015 M	4
CTABr 0.03 M	22
CTABr 0.05 M	31
CTABr 0.065 M	25
CTABr 0.085 M	23
CTABr 0.1 M	21

[a] At room temperature; reaction time = 3 h; TiO_2, 17 mg; substrate, 0.05 mmol; yields by GC; the material recovery (unreacted alcohol + formed aldehyde) is quantitative (≥90%); measured pH of water is 6.35 and that of aqueous TiO_2 dispersion is 4.35.

an increase of the yield up to a maximum and then a decrease. Maximum values occur at surfactant concentrations of 0.085 M for CTACl and 0.05 M for CTABr, where the yields are respectively 22% and 31%.

In CTABr the effect of pH was investigated and results are shown in Table 4. Using acidic conditions the product yield increases and best results are obtained with HCl at formal pH 1 (54% yield), rather than at pH 0 or 2. The nature of the acid itself, anyway, seems quite important in surfactant solutions. In particular, the use of HBr leads to a worse product yield (25% yield at pH 1) than in the absence of acid (31%) and with respect to HCl (54%). The experiment carried out in CTABr + NaCl 0.1 M clearly shows that the association of the anion to the micellar surface leads to a decreased product yield (17%), which is halved with respect to the reaction in the absence of NaCl. Therefore, the acid effect in micelles of CTABr is even better, if the data in aqueous HCl are compared with those obtained in the presence of NaCl. In CTABr with HCl 0.1 M different surfactant concentrations were monitored, as reported in Table 4. The yield reached the highest value in the 0.03–0.05 M range (ca. 55%).

The effect of surfactants of different charge type upon reaction yield was tested and results are reported in Table 5 where zwitterionic and anionic surfactants were used. Zwitterionic amine-oxide surfactant DDAO has almost no effect, whereas zwitterionic sulfobetaine surfactant SB3-14 affects positively the reaction. The surfactant concentration effect has the same behavior observed for cationic surfactants. In particular, for SB3-14, the maximum value obtained is at [surfactant] = 0.015 M with yield of 42%. A modification in the covalent structure of sulfobetaine surfactant head-group was introduced and SBPr3-14 was tested: the yield in aldehyde decreases with respect to the use of SB3-14 and the maximum value is 25%, at [surfactant] = 0.005 M. The reaction was also carried out in the presence of the anionic surfactant SDBS: also in this case the yield in aldehyde varies with surfactant concentration, with maximum yield of ca. 23% reached at [surfactant] = 0.065 M.

Table 4
Photocatalytic oxidation of 4-dodecyloxybenzyl alcohol (**1**) in presence of TiO_2 in aqueous solutions of CTABr in various conditions.[a]

[CTABr], M	Reaction medium	4-dodecyloxybenzaldehyde (mol %)
0.05	H_2O	31
0.05	HCl 0.01 M	42
0.007	HCl 0.1 M	18
0.011	HCl 0.1 M	28
0.015	HCl 0.1 M	44
0.03	HCl 0.1 M	55
0.05	HCl 0.1 M	54
0.065	HCl 0.1 M	50
0.1	HCl 0.1 M	44
0.05	HCl 1 M	30
0.05	HBr 0.1 M	25
0.05	NaCl 0.1 M	17

[a] At room temperature; reaction time = 3 h; TiO_2, 17 mg; substrate, 0.05 mmol; yields by GC; the material recovery (unreacted alcohol + formed aldehyde) is quantitative (≥90%); measured pH of water is 6.35 and that of aqueous TiO_2 dispersion is 4.35.

Table 5
Photocatalytic oxidation of 4-dodecyloxybenzyl alcohol (**1**) in presence of TiO_2 in aqueous solutions of different zwitterionic and anionic surfactants.[a]

Reaction medium	4-dodecyloxybenzaldehyde (mol %)
DDAO, 0.0001 M	2
DDAO, 0.0056 M	5
DDAO, 0.015 M	7
SB3-14, 0.005 M	22
SB3-14, 0.015 M	42
SB3-14, 0.05 M	35
SB3-14, 0.1 M	25
SB3-14, 0.03 M[b]	8
SBPr3-14, 0.0005 M	1
SBPr3-14, 0.005 M	25
SBPr3-14, 0.015 M	17
SBPr3-14, 0.05 M	6
SBPr3-14, 0.1 M	5
SDBS, 0.035 M	5
SDBS, 0.05 M	16
SDBS, 0.065 M	23
SDBS, 0.1 M	13

[a] At room temperature; reaction time = 3 h; TiO_2, 17 mg; substrate, 0.05 mmol; yields by GC; the material recovery (unreacted alcohol + formed aldehyde) is quantitative (≥90%); measured pH of water is 6.35 and that of aqueous TiO_2 dispersion is 4.35.

[b] In presence of HCl, 0.1 M.

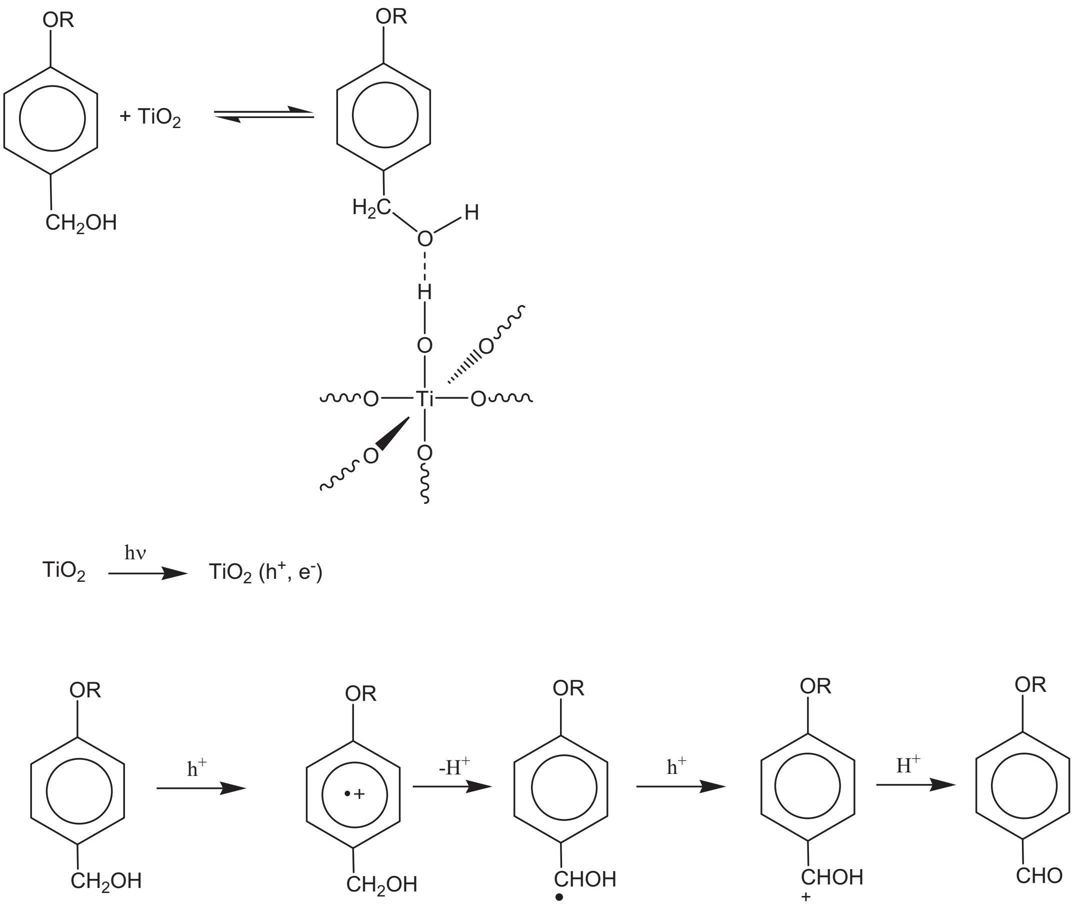
Some experiments have been also performed in the presence of SDS but, at low concentration ($\cong 10^{-3}$ M), the aldehyde yield is negligible and, as reported [8b], at concentrations higher than cmc this surfactant is degraded by UV light.

4. Discussion

Both substrates **1** and **2** react in CH_3CN giving the corresponding aldehyde according to a previously reported mechanism [12]. In particular, as reported in Scheme 3, the substrate is preadsorbed through a hydrogen bond interaction between the lone pairs of alcoholic oxygen and the hydrogen of the OH groups on the semiconductor surface; then it is oxidized by the photogenerated hole (h^+) giving a cation radical that, subsequently, deprotonates; the formed benzylic radical gives the corresponding aldehyde through a further oxidation step. The minor reactivity of **1** with respect to **2** (see Table 1) can be ascribed to a less effective adsorption of the alcohol **1** on the TiO_2 surface, probably because of the longer hydrocarbon chain that hinders the above hydrogen bond interaction.

As for the reaction in water, only alcohol **2** significantly reacts, through the same mechanism operative in CH_3CN [13], even if the aldehyde conversion in the aqueous medium is lower, probably due to the competitive photo-oxidation of water.

As concern the significant increase observed for **2** in water at pH 1, this behavior could be attributed to: (i) the increase of the oxidation potential of the hole in the valence band [18]; (ii) an higher adsorption extent of the substrate onto TiO_2, due to a stronger



Scheme 3. Photo-oxidation mechanism.

hydrogen bond interaction between the lone pairs of alcoholic oxygen and the hydrogen linked to the positively charged oxygen of H_2O^+ formed in acidic condition at the TiO_2 surface; (iii) an increase of adsorption sites due to the higher surface area of TiO_2, related to the fact that positively charged TiO_2 particles (see (ii)) repel each other (lower agglomeration) [12c].

Regarding the photo-oxidation of substrate **1** in water, it has been shown that this reaction significantly occurs in the presence of surfactants. To justify the observed phenomenon, at first we have evaluated the interaction between TiO_2 surface and the surfactant through conductivity measurements. The collected data (Table 2 and Fig. 1) neither prove or exclude that monomeric surfactant interact with TiO_2 particle, but they are clearly consistent with the idea that micelles are formed both in the presence and in the absence of TiO_2 and are rather similar in these two conditions. Therefore we may say that the reaction takes place in solution in the presence of micelles of the various surfactants, because the concentrations we used are always higher than their cmcs.

On the basis of geometric considerations we may exclude that particles of TiO_2 are kept inside a micelle: in fact diameters of TiO_2 particles are in the range 25–85 nm [19] and, therefore, are bigger by a factor higher than 10 with respect to the mean diameters of micelles, which is ca. 2–3 nm [20]. On the other hand, we may envisage that various micelles can go around a particle of TiO_2 [8b,21]. It must be observed that substrate **1**, which has an amphiphilic nature, can co-micellize. The interaction between micelles and a TiO_2 particle is probably driven by the co-micellized substrate, because it is known that the OH moiety of the substrate forms an hydrogen bond with the TiO_2 particle surface (see above). The reaction can take place only if the co-micellized substrate is adsorbed on the TiO_2 particle surface. Therefore we may think that the substrate, water insoluble, is solubilized in the micellar aggregates and transported with it close to the particle surface, where reaction occurs. In particular, we suggest that co-micellized alcohol **1**, adsorbed on TiO_2, is photo-oxidized to the co-micellized aldehyde. The co-micellized aldehyde could be then released from the TiO_2 surface, as it is less adsorbed on the semiconductor than co-micellized **1**.

On the basis of the above discussion we may explain the surfactant concentration effect, generally observed in solutions of the considered surfactants. Initially the aldehyde yield increases with the surfactant concentration and then, after a certain concentration which varies with the nature of the surfactant, it decreases. We may think that the increase of the surfactant concentration leads to an increase of the number of substrate molecules solubilized in micelles, which can be transported close to the TiO_2 particle surface where they react. We suggest that after a certain surfactant concentration a further increase of micelles involves a decrease of co-micellized **1** at the surface of TiO_2, slowing the reaction. In fact, at this surfactant concentration, the competitive partition between the co-micellized substrate **1** adsorbed on TiO_2 (where reaction occurs) and the co-micellized substrate in the bulk should become crucial; the increase of micelles moves the above equilibrium towards the aggregate in the bulk, more and more limiting the favorable kinetic effect of the surfactant.

As regards the effect of changes in the surfactant structure, we observe that there is no simple relation with the charge type. For example, the cationic CTAOMs and the zwitterionic DDAO and also the anionic SDS do not affect reaction.

Apart from the charge, the maximum values of the aldehyde yields in Tables 3 and 5 are, in the order, those obtained in the presence of SB3-14 > CTABr > CTACl ≈ SDBS ≈ SBPr3-14, therefore the best system is the zwitterionic sulfobetaine surfactant SB3-14. We could relate the different surfactant effect to the maximum number of substrate molecules that each kind of surfactant micelle can transport close to TiO_2. This depends on the solubilization ability of the micelle vs substrate **1**, and it also depends on the micelle number that approaches the TiO_2 particle surface. In fact, association of substrate **1** to surfactant aggregates was measured to elucidate if a different association extent of it in different surfactants can influence the product yield. In our experimental conditions the determination of the binding constants solute–micelles seemed not adequate. In fact reliable values of binding constants are generally obtained provided that the solute is not very hydrophobic, that the amphiphile is in big excess over substrate (this is referred as "kinetic conditions"), and that amphiphile concentration is well above the cmc [22]. Two conditions are not fulfilled in our case, because we have a hydrophobic substrate and because the ratio surfactant/substrate is rather low, ranging from 1:1 to ca. 20:1. Therefore we carried out experimental measures of substrate solubilization in different surfactant solutions, in conditions similar to those used for reaction. In surfactant solutions 0.05 M the solubilization of substrate 1 changes with surfactant nature: it is 7.5 mM, 4.9 mM and 3.6 mM in SB3-14, SBPr3-14 and CTABr respectively. The head group bulk effect is consistent with measured values of K_S for phenethylbromide in cetyltrialkylammonium hydroxide surfactants [23].

Besides, on the basis of electrostatic considerations, we may argue that neutral micelles do not repel each other when close together at the TiO_2 particle surface. Therefore the number of neutral micelles (and therefore the number of substrate molecules) around TiO_2 can be higher than the number of ionic micelles.

Similar considerations can account for the different effect of the various cationic surfactants. In fact, aldehyde yields increase with decreasing ionization degree, α, which are 0.25, 0.33 and 0.50 for CTABr, CTACl and CTAOMs, respectively [24]. As regards zwitterionic surfactant SBPr3-14, less efficient than SB3-14 (see Table 5), we can ascribe this effect to the observed decrease of substrate **1** solubilization in SBPr3-14 surfactant solutions.

As regards the pH effect, it is different in various surfactants solutions (see Table 4). In CTABr a shift to acidic pH improves the aldehyde yield for the reaction of substrate **1**; this effect can arise from the reasons discussed above for the reaction in water of **2**, although in the presence of micelles also the nature of the acid itself plays an important role, due to anion specific effect. In particular, bromide is known to be strongly associated to the micellar cationic surface, more than chloride [25] and, therefore, the micro-environments provided by the two systems, CTABr + HBr and CTABr + HCl, are different (actually, even from a visual point of view, the first system is not limpid, while the second is). On the contrary, in SB3-14 a shift to acidic pH decreases significantly the aldehyde yield. We may relate the decreased yield to a change of sulfobetaine micelle surface charge from neutral to anionic, due to the preferential micellar association with anions rather than with protons [26–28]. As already observed, charged micelles repel each other more than non-charged ones.

5. Conclusion

The TiO_2 photosensitized oxidation in water of 4-dodecyloxybenzyl alcohol (**1**), an insoluble substrate, to 4-dodecyloxybenzaldehyde does not occur but this reaction is observed in aqueous solutions of certain surfactants at concentrations higher than cmc. The reaction rate is strongly dependent on the nature of the surfactant, with micellar aggregates and their properties, as micellar ionization, playing a main role. Effects of surfactant concentration were studied in neutral and, where possible, in acidic conditions. We suggest that the increase of the surfactant concentration leads to an increase of the number of substrate molecules solubilized in micelles (through co-micellization), which can be transported close to the TiO_2 particle surface where **1** reacts. After a certain concentration, which varies with the nature of the surfactant, the presence of the competitive partition between the co-micellized substrate **1** adsorbed on TiO_2 (where reaction occurs) and the co-micellized substrate in the bulk tends to limit more and more the beneficial kinetic effect of the surfactant. The surfactant SB3-14 0.015 M gives the best performance in terms of product (aldehyde) yield (42%). A better yield (55%) is obtained with CTABr 0.05 M + HCl 0.1 M.

Acknowledgements

This work was funded by MIUR (Ministero dell'Istruzione, dell'Università e della Ricerca Scientifica), Italy (PRIN 2008, grant number 2008AZT7RK_002) and by Fondazione della Cassa di Risparmio di Perugia, Italy (2009.010.0355).

References

[1] U.I. Gaya, A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems, J. Photochem. Photobiol. C: Photochem. Rev. 9 (2008) 1–12.

[2] E. Pelizzetti, C. Minero, V. Maurino, A. Sclafani, H. Hidaka, N. Serpone, Photocatalytic degradation of nonylphenol ethoxylated surfactants, Environ. Sci. Technol. 23 (1989) 1380–1385.

[3] H. Hidaka, J. Zhao, E. Pelizzetti, N. Serpone, Photodegradation of surfactants. 8. Comparison of photocatalytic processes between anionic sodium dodecylbenzenesulfonate and cationic benzyldodecyldimethylammonium chloride on the TiO_2 suruface, J. Phys. Chem. 96 (1992) 2226–2230.

[4] H. Hidaka, K. Nohara, K. Ooish, J. Zhao, N. Serpone, Photodegradation of surfactants. XV: formation of SO_4^{2-} ions in the photooxidation of sulfur-containing surfactants, Chemosphere 29 (1994) 2619–2624.

[5] H. Tada, H. Matsui, F. Shiota, M. Nomura, S. Ito, M. Yoshihara, K. Esumi, Hetero-supramolecular photocatalysis: oxidation of organic compounds in nanospaces between surfactant bilayers formed on TiO_2, Chem. Commun. 16 (2002) 1678–1679.

[6] D. Fabbri, A. Bianco Prevot, E. Pramauro, Kinetic effects of SDS on the photocatalytic degradation of 2,4,5-trichlorophenol, Appl. Catal. B: Environ. 49 (2004) 233–238.

[7] D. Fabbri, A. Bianco Prevot, E. Pramauro, Effect of surfactant microstructure on photocatalytic degradation of phenol and chlorophenol, Appl. Catal. B: Environ. 62 (2008) 21–27.

[8] (a) T. Pernyeszi, I. Dékány, Photocatalytic degradation of hydrocarbons by bentonite and TiO_2 in aqueous suspensions containing surfactants, Coll. Surf. A: Physicochem. Eng. Aspects 230 (2004) 191–199;
(b) S. Horikoshi, D. Minami, S. Ito, H. Sakai, D. Kitamoto, M. Abe, N. Serpone, Molecular dynamics simulations of adsorption of hydrophobic 1,2,4-trichlorobenzene (TCB) on hydrophilic TiO_2 in surfactant emulsions and experimental process efficiencies of photo-degradation and -dechlorination, J. Photochem. Photobiol. A: Chem. 217 (2011) 141–146.

[9] M. Hudlicky, Oxidations in Organic Chemistry, American Chemical Society, Washington DC, 1990.

[10] W.J. Mijs, C.R.H.I. De Jonge (Eds.), Organic Synthesis by Oxidation with Metal Compounds, Plenum Press, New York, 1986.

[11] R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidation of Organic Compounds, Academic Press, New York, 1981.

[12] (a) L. Amori, T. Del Giacco, C. Rol, G.V. Sebastiani, Photooxidation of benzyl alcohols sensitized by TiO_2 in CH_3CN in the presence of Ag_2SO_4. Kinetic evidences for the involvement of adsorption phenomena, J. Chem. Res. (S) (1998) 644–645;
(b) M. Bettoni, T. Del Giacco, C. Rol, G.V. Sebastiani, Dark adsorption equilibrium constants of benzylic derivatives on TiO_2 and their implications in the sensitised heterogeneous photooxidation, J. Chem. Res. (S) (2003) 415–417;
(c) M. Bettoni, T. Del Giacco, C. Rol, G.V. Sebastiani, True quantum yields and asorption constants as tools for a mechanistic study of the TiO_2-sensitized photooxidation of benzylic derivatives, J. Photochem. Photobiol. A: Chem. 163 (2004) 481–487;
(d) T. Del Giacco, M. Ranchella, C. Rol, G.V. Sebastiani, Photo-oxidation of some benzylic alcohols sensitized by colloidal TiO_2 in CH_3CN. A kinetic mechanistic study through quantum yield determinations, J. Phys. Org. Chem. 13 (2000) 745–751;
(e) R. Palombari, M. Ranchella, C. Rol, G.V. Sebastiani, Oxidative photoelectrochemical technology with Ti/TiO_2 anodes, Sol. Energy Mater. Sol. Cells 71 (2002) 359–368;
(f) M. Ranchella, C. Rol, G.V. Sebastiani, The photoelectrochemical oxidation of benzyl derivatives at Ti/TiO_2 anodes. A mechanistic approach through

current efficiency and density measurements, J. Chem. Res. (S) (2002) 239–241.

[13] M. Bettoni, T. Del Giacco, F. Elisei, C. Rol, G.V. Sebastiani, Evidences in favour of a single electron transfer (SET) mechanism in the TiO_2 sensitized photooxidation of α-hydroxy- and α,β-dihydroxybenzyl derivatives in water, Phys. Chem. Chem. Phys. 12 (2010) 5425–5430.

[14] F. Del Rosso, A. Bartoletti, P. Di Profio, R. Germani, G. Savelli, A. Blaskò, C.A. Bunton, Hydrolysis of 2,4-dinitrophenyl phosphate in normal and reverse micelles, J. Chem. Soc. Perkin Trans. 2 (1995) 673–678.

[15] L. Brinchi, P. Di Profio, R. Germani, G. Savelli, N. Spreti, C.A. Bunton, Effect of micellar head group structure in the spontaneous hydrolysis of methylnaphtalene-2-sulfonate. The role of perchlorate ion, J. Chem. Soc. Perkin Trans. 2 (1998) 361–364.

[16] H.C. Evans, Alkyl sulfates. I. Critical micelle concentrations of the sodium salts, J. Chem. Soc. 80 (1956) 579–586.

[17] P. Mukerjee, K.L. Mysels, Critical Micelle Concentrations of Aggregate Surfactant Systems, National Bureau of Standards, Washington DC, 1970.

[18] P.V. Kamat, What makes semiconductor colloids unique as photocatalysts? Spectrum (1994) 14–20.

[19] T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, Morphology of a TiO_2 photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases, J. Catal. 203 (2001) 82–86.

[20] D.W. Gruen, The packing of amphiphile chains in a small spherical micelle, J. Colloid Interface Sci. 84 (1981) 281–283.

[21] H. Li, C.P. Tripp, Spectroscopic identification and dynamics of adsorbed cetyltrimethyl ammonium bromide structures on TiO_2 surfaces, Langmuir 18 (2002) 9441–9446.

[22] G. Savelli, R. Germani, L. Brinchi, Reactivity control by aqueous amphiphilic self-assembling systems, in: J. Texter (Ed.), Reactions and Synthesis in Surfactant Systems, Marcel Dekker, New York, 2001, pp. 175–246.

[23] L. Brinchi, P. Di Profio, R. Germani, G. Savelli, C.A. Bunton, A quantitative analysis of the effects of head group bulk on S_N2 and E2 reactions in cationic micelles, Langmuir 13 (1997) 4583–4587.

[24] P. Baglioni, E. Braccalenti, E. Carretti, R. Germani, L. Goracci, G. Savelli, M. Tiecco, Surfactant-based photorheological fluids: effect of the surfactant structure, Langmuir 25 (2009) 5467–5475.

[25] R. Bacaloglu, C.A. Bunton, F. Ortega, Micellar enhancement of rates of S_N2 reactions of halide ions. The effect of headgroup size, J. Phys. Chem. 93 (1989) 1497–1502.

[26] M. Da Silva Baptista, I. Cuccovia, H. Chaimovich, M.J. Politi, W. Reed, Electrostatic properties of zwitterionic micelles, J. Phys. Chem. 96 (1992) 6442–6449.

[27] N. Kamenka, M. Corro, Y. Chevalier, H. Levy, R. Zana, Aqueous solutions of zwitterionic surfactants with varying carbon number of the intercharge group. 2. Ion binding by the micelles, Langmuir 11 (1995) 4234–4240.

[28] P. Di Profio, R. Germani, G. Savelli, G. Cerichelli, M. Chiarini, G. Mancini, C.A. Bunton, N.D. Gillitt, Effects of headgroup structure on incorporation of anions into sulfobetaine micelles. Kinetic and physical evidence, Langmuir 14 (1998) 2662–2669.