

Effects of Water, Salt Water, and Silicone Overcoating of the TiO₂ Photocatalyst on the Rates and Products of Photocatalytic Oxidation of Liquid 3-Octanol and 3-Octanone

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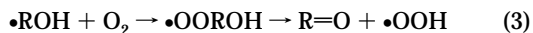
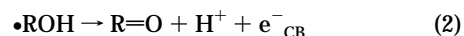
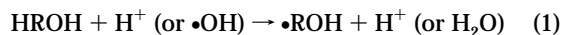
The environment of the TiO₂ photocatalyst affects the rate and the ratio of products generated in the photocatalytic oxidation of liquid 3-octanol and 3-octanone. The rates and products were determined with two photocatalysts, one directly solution-contacting and hydrophilic, the other embedded in a poly(methylsiloxane) and hydrophobic: in the neat organic reactant, without added water; with added water; and with NaCl (0.5 M) in the water. 3-Octanone was oxidized to CO₂ and to two organic phase extracted products *n*-hexanoic acid and *n*-pentanal. The organic phase extracted initial oxidation products of 3-octanol were 3-octanone, *n*-hexanal, and *n*-pentanal. The CO₂ evolution rate was highest in neat 3-octanone when the hydrophilic photocatalyst was in direct contact with the liquid reactant, in which the catalyst particles were uniformly dispersed. When water was added, this photocatalyst resided at the liquid–liquid interface, and the rate of CO₂ evolution was reduced. The rate was further reduced when NaCl was added. When the TiO₂ was embedded in the hydrophobic silicone, the photocatalyst remained dispersed in the organic phase, and the reaction was not inhibited by NaCl. The rate of CO₂ formation now exceeded that for the hydrophilic catalyst.

Introduction

We show in this article that the environment of the TiO₂ photocatalyst affects the yields and product ratios in the photocatalytic oxidations of 3-octanone and 3-octanol. Photocatalyzed oxidation reactions on TiO₂ have been extensively studied, particularly in the context of stripping of pollutants and more recently also in the context of maintenance of clean surfaces. In these reactions, the photogenerated holes react with adsorbed species, such as water or organic reactants, while the photogenerated electrons react with adsorbed oxygen (1, 2). The hole reactions' initial products are adsorbed OH radicals and organic radicals. The electron reaction produces hydroperoxy (•OOH) radicals. The reaction mechanisms and intermediates of these reactions have also been extensively studied (3–8).

Secondary alcohols are oxidized to ketones by a two-electron process where one electron is transferred to the OH

radical and a second electron is injected into the conduction band of the semiconductor, a process similar to that encountered in the "current doubling" oxidations on semiconducting electrodes (reactions 1 and 2) (9–13). A second route to a ketone involves hydrogen abstraction by the OH radical, formation of an organic radical, its combination with O₂ (13, 15, 16) leading to an organoperoxy radical and release of an •OOH radical (reactions 1 and 3) (13, 14).



In an earlier study of photocatalytic oxidation of 8-carbon aliphatic compounds on salt water using buoyant photocatalyst coated microbubbles, it was found that when the catalyst was bound by embedding it in a highly cross-linked hydrophobic silicone [a poly(methylsiloxane) formed by hydrolysis of methyltrimethoxysilane and condensation of the resulting silanol], the rates of oxidation were usually higher than those for directly solution-contacting hydrophilic TiO₂ that was bound through a thermal process (17, 18). Embedding of the photocatalyst in silicone prevented access of oxidation-inhibiting chloride ions to the TiO₂ surface.

Here we report on the effects of added water and salt on the rates and products distributions of photocatalytic oxidation of 3-octanol and of 3-octanone on silicone-embedded hydrophobic TiO₂ and on hydrophilic, solution-contacting TiO₂ in a single liquid organic phase, consisting of the reactant and its products; in a two phase system, with water added to the organic reactant; and in the two phase system with NaCl (0.5 M) dissolved in the aqueous phase.

Experimental Section

Aluminosilicate ceramic microbubbles of 0.66 g/cm³ density (Cenolites, C-type) were obtained from Pozzolan Industries Limited, Milton, Queensland, Australia. Part of these were coated with TiO₂ by thermal bonding, whereby a hydrophilic, directly solution contacting TiO₂ layer was produced on the bubbles (19). The silicone bubbles with hydrophobic silicone-embedded TiO₂ were formed by the earlier described low-temperature process (19) modified as follows: 15 mL of MTMOS (methyltrimethoxysilane) was mixed with 15 mL of ethanol and 1.8 mL of 2 M HCl and allowed to hydrolyze for 15 min. The solution was diluted with an equal volume of ethanol, then 50 g of Cenolites and 10 g of TiO₂ (Degussa P25) were added to form, upon mixing, a thick paste. The paste was heated in air at 120 °C for 48 h. The resulting hydrophobic bubbles were loosened, sieved, etched in 1 M HCl for 30 min, washed with deionized water, and dried at 100 °C.

Photocatalytic oxidations were performed in 350 mL, 8 cm diameter cylindrical Pyrex reactors. The irradiance by 300–400 nm [365 nm (max)] light was 35 W/m². Before the reaction, 1 g of beads, 5 mL of reactant, and 60 mL of deionized water (with or without NaCl) were mixed in the reactor, which was flushed with a mixture of "zero air" (79% N₂/21% O₂), then sealed. The reactor was placed on an 120 rpm orbit shaker and exposed for 16 h. When the reactions were carried out without adding water, only 1 g of the bubbles and 5 mL of the reactant were added.

The amount of CO₂ generated was measured with a Beckman Industrial Model 870 CO₂ analyzer. Gas samples

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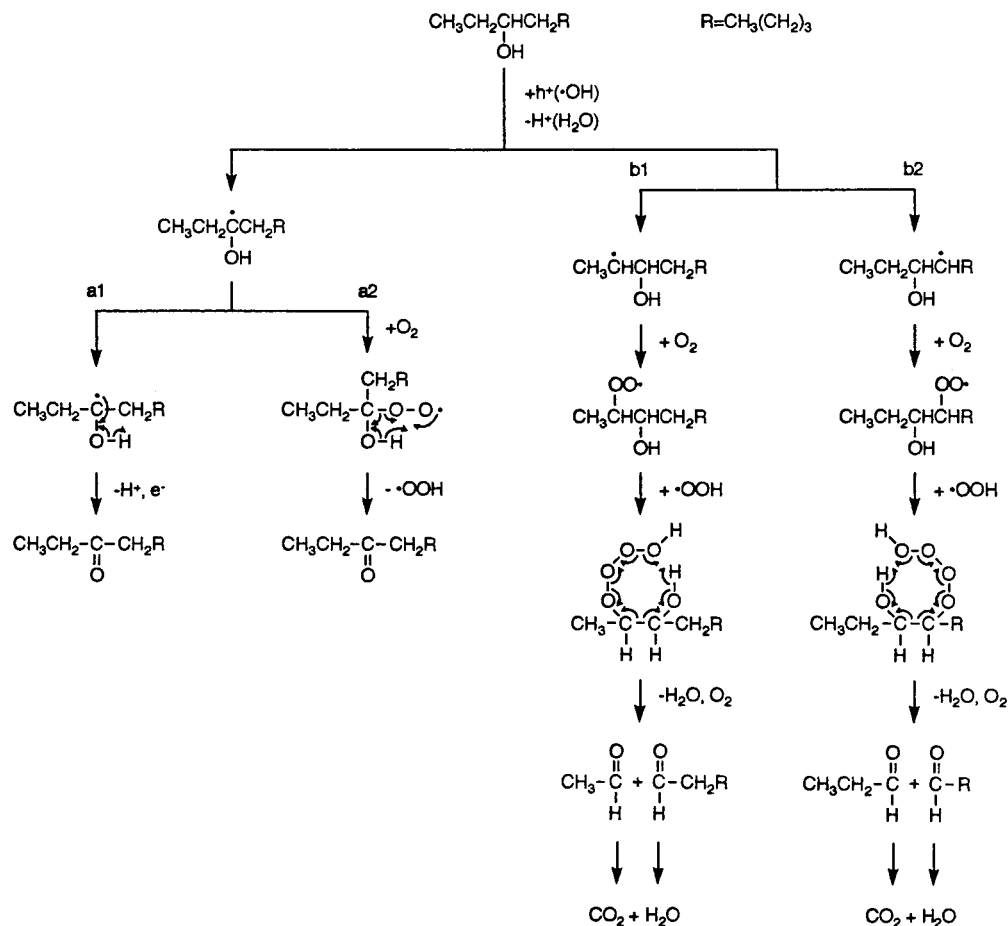


FIGURE 1. Possible routes of photocatalytic oxidation of 3-octanol.

TABLE 1. Yields of the Products in the Photocatalytic Oxidations of 3-Octanol and 3-Octanone on Water, and the Effect of Addition of 0.5 M NaCl^a

products	bare TiO ₂		silicone-bound TiO ₂	
	H ₂ O	0.5 M NaCl	H ₂ O	0.5 M NaCl
(a) 3-Octanol				
CO ₂	1.2	0.50	0.72	0.72
3-octanone	0.35	0.35	0.77	0.93
<i>n</i> -hexanal	0.22	0.13	0.33	0.27
<i>n</i> -pentanal	0.13	0.081	0.16	0.15
hexanoic acid	trace	trace	0.081	0.081
pentanoic acid	trace	trace	0.028	0.030
(b) 3-Octanone				
CO ₂	2.3	1.1	1.8	2.1
<i>n</i> -pentanal	0.10	0.092	0.10	0.089
hexanoic acid	0.05	0.11	0.18	0.27
pentanoic acid	0.03	0.06	0.13	0.18

^a Results in moles of product per 100 einsteins.

of 5 mL were withdrawn from the reactor with an air-tight gas syringe and injected into a loop connected to the analyzer through a pump. The products in the organic phase were analyzed by GC using a Tracor 540 gas chromatograph with a flame ionization detector and 30 m × 0.53 mm HP-INNOWax capillary column, with helium as carrier gas. The temperature of the column was raised from 40 to 200 °C at a rate of 15 °C/min. The temperatures of the injector and the detector were maintained at 250 °C. The products were identified by measuring their retention times; then measuring the retention times of standard samples of the chemicals assumed to be the products, confirming that the two retention times were identical; then coinjecting a mixture containing

TABLE 2. Yields of the Products in the Photocatalytic Oxidations of 3-Octanol and 3-Octanone on Water and without Water^a

products	bare TiO ₂		silicone-bound TiO ₂	
	with H ₂ O	without H ₂ O	with H ₂ O	without H ₂ O
(a) 3-Octanol				
CO ₂	1.2	1.3	0.72	0.90
3-octanone	0.35	1.2	0.77	0.95
<i>n</i> -hexanal	0.22	0.68	0.33	0.62
<i>n</i> -pentanal	0.13	0.55	0.16	0.45
hexanoic acid	trace	0.12	0.081	0.10
pentanoic acid	trace	0.066	0.028	0.045
(b) 3-Octanone				
CO ₂	2.3	3.5	1.8	1.9
<i>n</i> -pentanal	0.10	0.14	0.10	0.13
hexanoic acid	0.05	0.45	0.18	0.26
pentanoic acid	0.03	0.28	0.13	0.23

^a Results in moles of product per 100 einsteins.

both the product and the standard sample and confirming the absence of any variation in retention time or peak-shape. The amount of each of the products was quantified by measuring the peak height produced by a known amount of the diluted standard sample and by using this height for calibration. Each sample was analyzed twice. The difference between the results of any of the assay pairs was less than 10%.

3-Octanol and 3-octanone were purchased from Aldrich and used without further purification. The 3-octanol contained a small amount of 3-octanone that was gas chromatographically detected and assayed. The 3-octanone

contained hexanoic acid and pentanoic acid that were similarly assayed. The data were corrected for the presence of these impurities.

Results

Both the hydrophilic and the hydrophobic photocatalyst coated microbubbles were buoyant on water. In the hydrophilic bubbles, the TiO_2 catalyst coating directly contacted the liquid. In the hydrophobic bubbles, the TiO_2 catalyst was embedded in a highly cross-linked silicone that was permeable to the reactants and products, but not to NaCl. When mixed with the reactant and water, the hydrophilic bubbles resided at the interface between the water and the organic phase. The hydrophobic bubbles resided in the organic phase. The hydrophobic bubbles remained hydrophobic after extended use in the presence of either of the organic reactants but, in their absence, became hydrophilic on extended exposure.

The products of the photocatalytic air oxidations are shown for the two types of microbubbles in Table 1. In the absence of either photocatalyst or flux of UV photons, CO_2 was not produced from 3-octanol. When 3-octanol was photocatalytically oxidized on the bare, water-wetted TiO_2 beads, CO_2 was generated at a rate that was 1.6 times faster than that measured when the beads were coated with the silicone-embedded TiO_2 . The major product that accumulated in the organic phase was 3-octanone. Minor products included aldehydes and carboxylic acid produced by cleavage of the carbon chain. The amount of 3-octanone that accumulated in the organic phase when hydrophobic bubbles coated with the silicone-embedded TiO_2 were used was twice the amount that accumulated with the hydrophilic TiO_2 coated bubbles. The amounts of the aldehydes and carboxylic acids that accumulated were also higher.

CO_2 was generated much faster in the photocatalytic oxidation of 3-octanone than in the oxidation of 3-octanol. The rate of CO_2 generation from 3-octanone with the hydrophilic bubbles exceeded that with the hydrophobic ones by 20%. In the oxidation of 3-octanol, the rate for the hydrophilic bubbles was 60% greater than for the hydrophobic ones. *n*-Pentanal, *n*-hexanoic acid, and *n*-pentanoic acid were detected in the organic phase.

Upon adding NaCl (0.5 M) to the deionized water (Table 1), the amount of CO_2 generated from either of the two reactants with the hydrophilic bubbles was reduced by 60%, but the CO_2 yield was not reduced when the hydrophobic bubbles were used. As a result, the rate of CO_2 generation exceeded, when the hydrophobic bubbles were used, the rate observed with hydrophilic ones in the presence of 0.5 M NaCl, in agreement with Schwitzgebel et al. (17). While the CO_2 yield was greatly lowered by adding NaCl to the water, the yield of 3-octanone from 3-octanol was unchanged.

In order to assess the role of water, oxidations of the neat organic reactants were carried out with both types of bubbles. Now both the hydrophilic and the hydrophobic bubbles were dispersed uniformly in the organic phase. The results are shown in Table 2. More CO_2 was generated in all cases, especially in the reaction of 3-octanone on hydrophilic TiO_2 , and the yields of the organic products were also higher.

Discussion

The photocatalytic oxidation of 3-octanol may proceed along any of the four routes shown in Figure 1. Route a1 is relatively insensitive to the photocatalyst's environment while routes b1 and b2 are affected by the environment. The following postulated routes are consistent with the results. Routes a1 and a2 start with the abstraction of a hydrogen atom from the carbon atom with hydroxyl group. (Tables 1 and 2) In

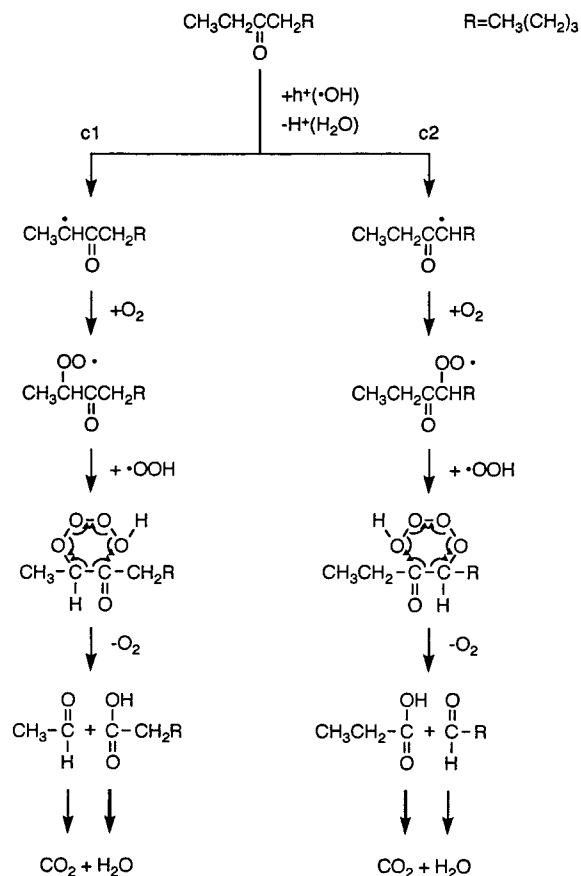


FIGURE 2. Possible routes of photocatalytic oxidation of 3-octanol.

route a1, the radical produced is converted into 3-octanone by injection of an electron into the conduction band of TiO_2 . In route a2, which we do not consider to be significant, the radical first combines with O_2 , then a hydroperoxyl radical is released. The reasons for electron injection being postulated as significant and $\cdot\text{OOH}$ release as insignificant are the following. Rehm et al. reported very fast electron injection ($\sim 10^{-12}$ s) from a photoexcited dye into the conduction band of the TiO_2 (20). If the hydrogen-abstracted radical is as reducing as the excited dye, the rate of route a1 is fast relative to any other, and this route dominates. Because injection does not involve any solution process and is faster than any recombination process, the rate and efficiency are not lowered by adding an inhibitor such as NaCl to the water-containing reaction mixture. If the hydrogen-abstracted radical is not highly reducing, then electron injection is unlikely. In this case, the radical reacts with O_2 to form an organoperoxy radical. Choi et al. (16) have found the bimolecular rate constant for a related reaction to be high [$k(\text{CH}_3)_2\text{CHO} + \text{O}_2 = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$]. However, the release of an OOH radical by the organoperoxy radical is slow. Bothe et al. reported a rate constant of only about 10^3 s^{-1} in a related system (14). Yamagata et al. (13) found that oxygen had little effect on the two electron oxidation, consistent with electron injection by the initially formed radical, and not with its combination with O_2 . As seen in Table 1, the yield of 3-octanone from 3-octanol was not affected by adding NaCl to the water-containing systems. This was the case whether the catalyst was hydrophilic and directly solution contacting, or silicone embedded and hydrophobic. Such independence of the environment of the photocatalyst and of the presence of electron-hole recombination enhancing inhibitors is expected only for route a1 and for this route only when the rate of the electron injection is rapid.

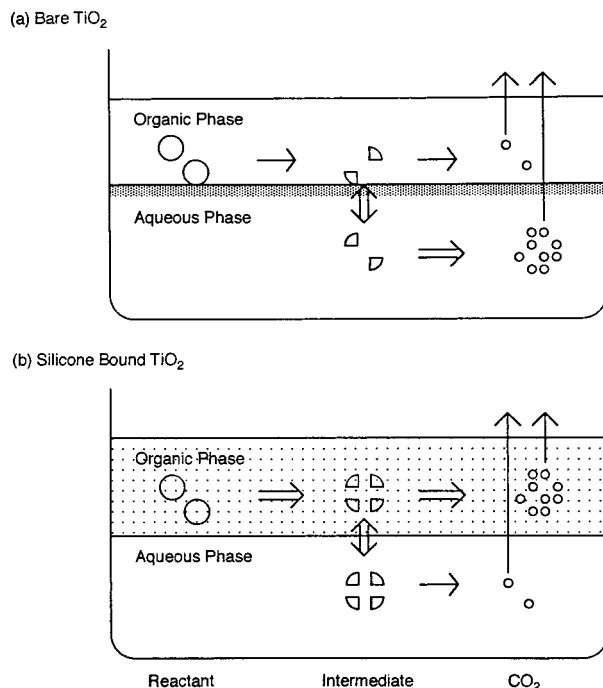


FIGURE 3. Schematic diagram of the distribution of the microbubbles, the reactants, the intermediate products, and the CO_2 for a system formed with microbubbles that are coated with a solution contacting hydrophilic TiO_2 layer and for a system formed with microbubbles coated with a hydrophobic silicone membrane in which the TiO_2 is embedded. The reactant is denoted by large circles; the intermediate product by four quarters of a circle; and carbon dioxide by small circles.

Postulated routes b1 and b2 start with abstraction of a hydrogen atom from the carbon atom next to the one with the OH function. The resulting radicals combine with O_2 , then with the hydroperoxyl radical, to form an organohydroperoxide intermediate that decomposes into two aldehydes, H_2O and O_2 . The aldehydes produced are oxidized to carboxylic acids that are subsequently oxidatively decarboxylated, generating CO_2 . *n*-Hexanal, an observed product, is formed through route b1, and *n*-pentanal, the second observed product, through route b2. Acetaldehyde from route b1 and propanal from route b2 are water soluble and, being water extracted, were not found in the analyzed organic phase. *n*-Hexanoic and *n*-pentanoic acids were produced by oxidation of *n*-hexanal and *n*-pentanal. Sitkiewitz et al. (21) and Loeff et al. (22) earlier proposed related aldehyde-involving routes for photocatalytic and X-ray radiolytic oxidations of aromatic compounds.

In the postulated reaction of 3-octanone, a hydrogen atom is abstracted mainly from the carbon next to the carbonyl group (Figure 2). The resulting radical reacts with dissolved O_2 to form an organoperoxy radical, which combines with a hydroperoxyl radical formed in the reaction of the photogenerated electron with O_2 . The resulting organohydroperoxide decomposes to a carboxylic acid, an aldehyde, and O_2 . The observed hexanoic acid and acetaldehyde are formed by route c1, and the observed *n*-pentanal and water-extracted propionic acid by route c2. Because carboxylic acids are formed directly from the organohydroperoxide (unlike in the oxidation of 3-octanol where aldehydes were formed) and because the acids are rapidly decarboxylated (23), CO_2 production from 3-octanone is faster than from 3-octanol.

Oxidation was more efficient in absence of added water (Table 2). Exclusion of water and ions from the catalyst

surface by its embedding in silicone was unnecessary for reaching high conversion rates, the silicone only reducing the number of available catalytic sites and thereby slowing the rates (Table 2). When water was added, the redistribution of the bubbles and the partition of products between the phases affected the yields. While the hydrophobic bubbles resided in the organic phase, the hydrophilic bubbles resided at the organic–water interphase, as shown schematically in Figure 3. Because the water-soluble products acetate, propionate, acetaldehyde, and propanal were extracted by the aqueous phase from the organic phase, addition of water reduced the rate of CO_2 generation. This rate was, however, not greatly reduced, because of the abundance of CO_2 precursors, like *n*-hexanoic and *n*-pentanoic acids, as well as *n*-hexanal and *n*-pentanal, in the organic phase.

That NaCl inhibits photocatalytic oxidations is well-known (24, 25). The reduced CO_2 generation rate when NaCl is added is attributed to chloride ion assisted recombination of the photogenerated electrons and holes (26). Adsorbed chloride is oxidized to adsorbed chlorine atoms by the holes, then reduced to chloride by the electrons. When the Cl^- anions were excluded from the TiO_2 surface by embedding the TiO_2 in a silicone that is impermeable to NaCl but is permeable to the reactants and products, the photocatalytic oxidations were no longer inhibited by added NaCl. Thus, for oxidative stripping of organic films on salt water and from surfaces subject to contamination by salt, the silicone embedded photocatalyst is preferred.

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