



## Photo-oxidation of benzyl alcohol under natural weathering conditions

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### Abstract

The photocatalytic oxidation of benzyl alcohol has been investigated by the following carbonyl compound formation. Measurements were made under natural weathering conditions (sunlight and oxygen) in the existence of titanium dioxide or sensitized titanium dioxide. Sensitization of titanium dioxide has been done by the impregnation of Riboflavin (RF), Safranin O (SO), Methyl red (MR), Eosin B (EB), and Methyl blue (MB) on anatase (Degussa P25). The photo-oxidation of benzyl alcohol was found to be fell in the sequence: Riboflavin > Safranin O > Naked TiO<sub>2</sub> > Methyl red > Eosin B > Methyl blue. The formation of benzaldehyde during the photocatalytic reaction has been studied by using FTIR, HPLC and spectrophotometric measurements.

*Keywords:* Photo-oxidation; Benzyl alcohol; Solar energy; Titanium dioxide

### 1. Introduction

The removal of environmental pollutants such as hazard organic compounds and environmental endocrine disruptors becomes a more interesting projects during the past two decades. Zhang et al. [1] showed that the pollutants caused serious diseases such as cancer, hormone deficiency, and bronchitis.

Over the last two decades, stable semiconductors with a large band gap, such as TiO<sub>2</sub> and ZnO have been used to photodegrade organic

environmental pollutants to convert them into harmless substances such as carbon dioxide [2–4].

Complete mineralization of different organic pollutants to carbon dioxide was demonstrated by Serpone et al. [5], using different oxidizing agents, and this process has been described as a member of the family processes known as advanced oxidation processes (AOPS). The authors described the principle advantage of the AOP approaches of water treatment as encouraging processes for the industrialized countries to use it in water purification processes such as decontamination, detoxification, decolorization, and deodorization.

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Mopper et al. [6] have shown that many of low molecular weight carbon compounds result from the irradiation of dissolved organic matter such as carbon monoxide, carbon dioxide, methanal, ethanal, ethanedial, propanone, 2-oxopropanal, and oxoethanoic and 2-oxopropanoic esters. The fragmentation of high molecular weight carbon compounds dissolved in water to carbon dioxide, gives a good achievement in detoxification of water. As a tool to remove the organic environmentally dangerous organic compounds, Pruden and ollis [7] have investigated the photofragmentation of these compounds using sunlight and  $\text{TiO}_2$ .

Sunlight was used instead of the free ultraviolet radiation to get rid of the free cyanide by adding phenol or hydrogen peroxide as oxidizing agents for the suspended  $\text{TiO}_2$  aqueous solution [8]. It was observed that the rate of photooxidation reaction depends upon the concentration of the cyanide ion and the oxidizing agent as well as the quantity of  $\text{TiO}_2$ , where as the kinetics of the reaction depends upon the concentration of the oxidizing agent and is independent upon the initial concentration of the ions or the mass of the catalyst.

Photofragmentation of some polynuclear aromatic compounds; such as naphthalene, anthracene, and fluorene; have been studied on the surface of  $\text{TiO}_2$  [9]. The investigation included studying the mechanism of the catalyzed photoreaction. Most semiconductors, especially that with a large band gap, are excited with ultraviolet light. An important method to extend the semiconductor's absorptive range, and thus enables the excitation to occur under normal weathering condition, is the photosensitization process. In photosensitization process, the sensitizer absorbs radiation in the visible range to yield an excited state of the sensitizer. The excited sensitizer injects an electron to the conduction band of the semiconductor. Sensitization processes may be done by direct addition of natural or artificial dyes to the large band gap semiconductors such as  $\text{TiO}_2$  and  $\text{ZnO}$ .

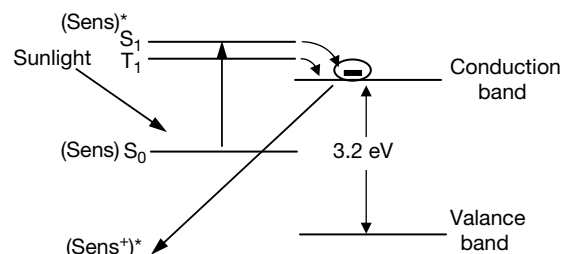


Fig. 1. The principle of charge injection from excited sensitizer into a conduction band of titanium dioxide.

Tsao and Eto [10] studied the effect of some natural photosensitizers on photolysis of some organic compounds. They reported that rose bengal and chlorophylline showed a great accelerating effect on the photodecomposition of cartap,  $S,S'$ -(2-dimethylaminotrimethylene) bis(thiocarbamate). They also concluded that the activity of the sensitizer is dependent upon many factors such as ultraviolet absorption of the sensitizer, wavelength of irradiation, the reaction media and the ultraviolet absorption by the substance. A great application of the idea of photosensitization is the utilization of visible light for degrading colored pollutants [11]. Photosensitization process could play a great vital role in detoxification and decolorization of industrial wastewater of textile factories, since 5% of the synthetic dyes are lost in waste streams during industrial processes [4,12–14]. Most of recent studies used visible light for irradiation [4,12–15].

In photosensitization process, which is defined as the conversion of light energy to chemical reactivity [16], a colored organic or inorganic dye or pigment is added to a semiconductor. The added sensitizer (Sens) absorbs light in to the visible range to yield an excited state of the sensitizer  $(\text{Sens})^*$ . The excited sensitizing dye molecule injects an electron from excited singlet ( $S_1$ ) or triplet ( $T_1$ ) states into the conduction band of the semiconductor [17]. Fig. 1 illustrates the principle of these processes.

In the present work, different types of organic dyes were added to  $\text{TiO}_2$  and the photocatalytic oxidation of benzyl alcohol was studied by using naked and sensitized anatase under

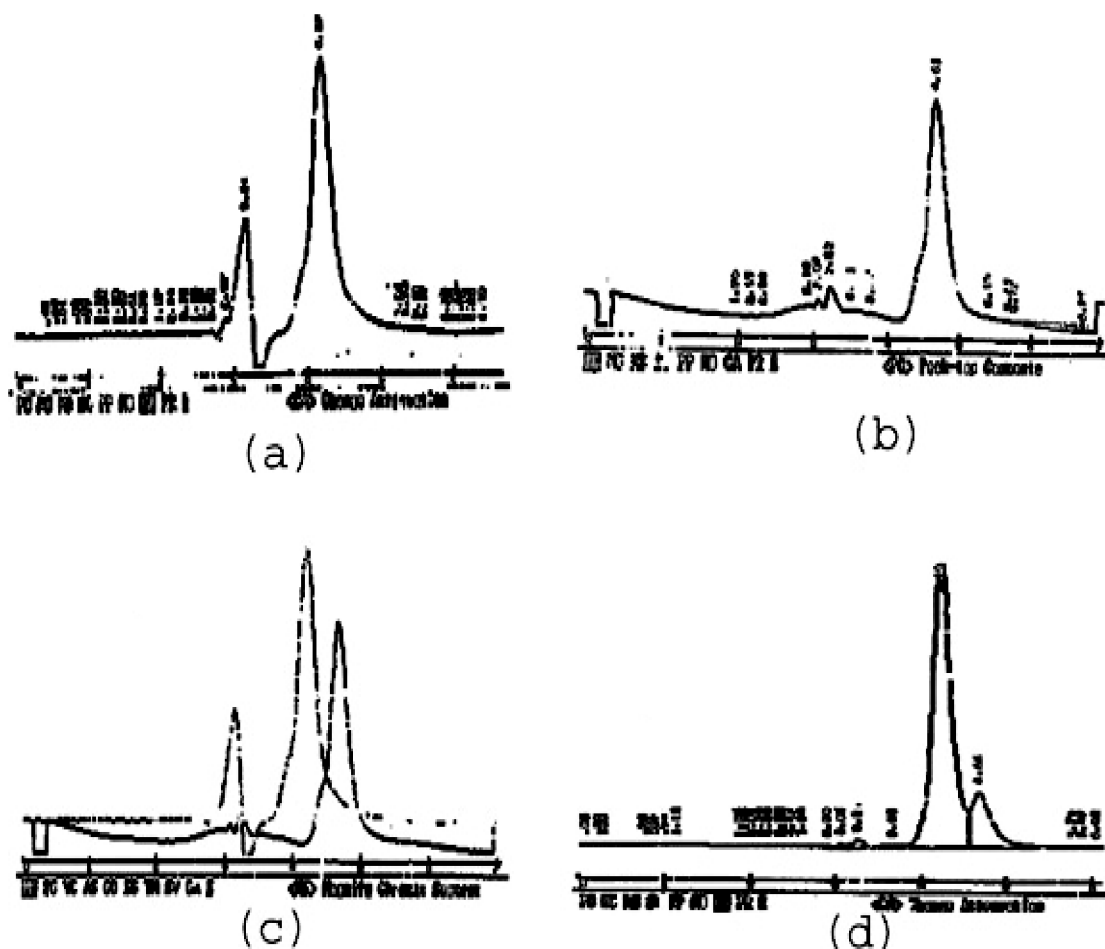


Fig. 2. Chromatographic spectra of HPLC analysis for (a) pure benzyl alcohol (b) pure benzaldehyde (c) 50% mixture of benzyl alcohol and benzaldehyde (d) benzaldehyde formed from the photocatalytic oxidation of benzyl alcohol on  $\text{TiO}_2$ .

natural conditions of weather with the addition of specific dyes to large band semiconductor such as  $\text{TiO}_2$  or  $\text{ZnO}$  with modified surface. This process played a vital role in the development of commercially solar cells [17], in which the photo-response of the large band semiconductor is extended to the visible region.

## 2. Experimental

### 2.1. Chemicals

Titanium dioxide powder (Degussa P25) with a surface area of  $50 \text{ m}^2 \text{ g}^{-1}$  was used as supplied.

All chemicals were obtained from BDH in highest available purity ( $\sim 99\%$ ). Sensitization of titanium dioxide has been done by impregnation method. One percent of anatase was added to alcoholic dye solution ( $1 \times 10^{-5} \text{ M}$ ). The suspension was purged with air with a flow rate of  $30 \text{ cm}^3 \text{ min}^{-1}$  with continuous stirring for 2 h at 298 K. Sensitized anatase particles were separated using Ganetzki T.S. centrifuge, and then washed thoroughly several times with ethanol until the supernatant became colorless. Sensitized anatase was dried under vacuum at 303 K for 4 h.

Table 1

IR Spectrum for photocatalytic oxidation of benzyl alcohol using TiO<sub>2</sub> sensitized with riboflavin and sun light for 75 min\*

Frequency (cm <sup>-1</sup> )	Intensity	Assignment
3398, 3300 and 3244	s	O–H (stretch), Intermolecular hydrogen bonded, benzyl alcohol and riboflavin.
3063 and 3030	w	C–H (stretch), aromatic.
2928	w	C–H (stretch), asymmetrical, CH <sub>2</sub> .
2872	w	C–H (stretch), symmetrical, CH <sub>2</sub> .
1954, 1875, 1813 and 1748	w	Combinations and overtones.
1693	w	C=O (stretch), aldehydic(*)
1599, 1495 and 1453	w-m	C=C (stretch), benzene ring, overlapped by CH <sub>2</sub> scissoring at 1471 cm <sup>-1</sup> .
1205	m	O–H (bend) and C–H (i.p. bend), monosubstituted benzene ring.
1015	s	C–O (stretch), primary alcohol substituted with C <sub>6</sub> H <sub>5</sub> and C–H (i.p. bend), aromatic
741 and 698	m	C–H (o.o.p bend), monosubstituted benzene ring

\*Indicates the formation of benzaldehyde.

## 2.2. Experimental Techniques

Experiments were conducted in September 2002, over continuous 10 days periods. All experiments were done at the floor of chemistry department building in an open atmosphere between 11.00 a.m. and 1.00 p.m. Sunlight illumination was carried out in a 150 cm<sup>3</sup> beaker containing 25 cm<sup>3</sup> of the sample, where the radiation was collected using converging lens with focal length of 10 cm. In all experiments, 20 mg of anatase was suspended in 25 cm<sup>3</sup> of benzyl alcohol. Periodically, 0.2 cm<sup>3</sup> samples of the reaction mixture were withdrawn using a syringe with a long pliable needle. These were centrifuged to separate the solid catalyst and the supernatant analyzed for identification of reaction products. Analyses were made by HPLC (fixing the wavelength of the UV at 254 nm), Type 6A supplied by Shimadzu or by FTIR, Type FTIR 8300, supplied by Shimadzu.

## 3. Results and Discussions

### 3.1. Preliminary experiments

These experiments were made to determine the conditions necessary for photocatalytic

activity. The reaction of benzyl alcohol under natural weathering condition was followed in the presence of sunlight radiation and naked TiO<sub>2</sub>, in the presence of sunlight and sensitized TiO<sub>2</sub>, in the presence of naked TiO<sub>2</sub> or sensitized TiO<sub>2</sub> with the absence of sunlight and in the presence of dye with the absence of TiO<sub>2</sub> and sunlight. The following results were obtained:

- 1) The only detected reaction product was benzaldehyde as identified by the following of HPLC and FTIR analysis, Fig. 2 and Table 1.
- 2) In the presence of naked or sensitized TiO<sub>2</sub> and sunlight, the benzaldehyde concentration increased linearly with irradiation time.
- 3) There was no dark reaction in the presence of naked or sensitized TiO<sub>2</sub>.
- 4) There was no reaction in the presence of sunlight and naked dye, i.e., in the absence of TiO<sub>2</sub>.

Table 1 indicates the formation of benzaldehyde by the appearance of the carbonyl group absorption peak (C=O stretch at 1693 cm<sup>-1</sup>). However, the disappearance of the aldehydic C–H stretch peaks at 2818 cm<sup>-1</sup> and 2737 cm<sup>-1</sup> asserts that the peaks were obscured by the 2872 cm<sup>-1</sup>

Table 2

Photoconversion of benzyl alcohol to benzaldehyde on naked and sensitized anatase at different temperatures

Time of irradiation (min)	$10^2 \times$ Benzaldehyde Concentration/mol dm <sup>-3</sup>					
	Type of Sensitizer					
	Riboflavin 316 K	Safranin O 317 K	Methyl red 318 K	Eosin O 320 K	Methyl blue 320 K	Naked TiO <sub>2</sub> 320 K
0	0	0	0	0	0	0
15	0.51	0.33	0.22	0.17	0.13	0.27
30	1.92	1.48	0.41	0.35	0.26	0.51
45	2.91	1.94	0.72	0.57	0.46	0.90
60	3.75	2.47	1.02	0.82	0.63	1.25
75	4.36	3.07	1.20	0.96	0.76	1.50
$10^6 \times$ rate /mol dm <sup>-3</sup> s <sup>-1</sup>	10.42	6.86	2.67	2.13	1.69	3.33

peak of benzyl alcohol due to the low concentration of the formed benzaldehyde.

### 3.2. Photocatalytic reactions

These experiments were carried out over the temperature range 316–321 K (as the temperature obtained due to the effect of sunlight). The results are given in Table 2 and plotted in Fig. 3.

The results indicate that sensitized anatase with riboflavin and safranin O has a higher activity than the naked one. This could be the

result of the addition of the sensitizer which enhanced the efficiency of the photocatalytic system and shifted the photo-response of TiO<sub>2</sub> to the visible region of the solar spectrum. Repeating the experiments with pre-used sensitized anatase with riboflavin and safranin gave a good reproducibility for photocatalytic reaction. However; with methyl red, Eosin B, and methyl blue, the sensitized anatase gave a lower reactivity. In addition, It was noticed that the color of these sensitizers became faint which could be referred to the formation of the leuco form [18].

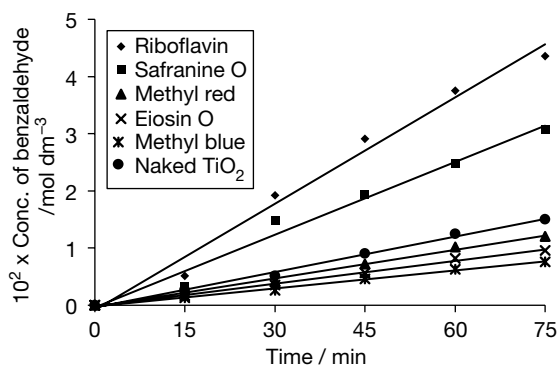


Fig. 3. Photocatalytic oxidation of benzyl alcohol using naked and sensitized TiO<sub>2</sub> under natural weathering conditions.

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