

Photocatalytic oxidation of selected aryl alcohols in acetonitrile[☆]

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Abstract

Photocatalytic oxidation of selected aryl alcohols (1–7) has been carried out by using anatase titanium dioxide catalyst. The main oxidation products were the corresponding aldehydes or ketones and acids, in addition to unidentified minor compounds. Kinetic studies revealed a second-order reaction rate for benzyl alcohol, as a model alcohol, photocatalytic oxidation. The suggested mechanism envisages electron–hole pair formation on the catalyst surface followed by oxidation–reduction reactions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalytic oxidation; TiO₂; Aryl alcohols

1. Introduction

Following the discoveries of Fujishima and Honda on water photolysis [1], considerable research work has been devoted to the investigation of photocatalytic electrochemistry [2]. The photochemical oxidation of water still remains one of the most serious problems in the solar splitting of water into oxygen and hydrogen [3,4]. This idea seems very interesting because about 50% of the solar radiation reaching the surface of the earth fall in the range 300–700 nm and can be used to drive a wide variety of photochemical reactions [5].

Semiconductor powders, mainly metal oxides [6,7] suspended in solution or as supported thin film have been used to carry out heterogeneous photocatalytic processes for production of useful chemicals [8–11] and treatment of wastes and pollutants through degradation or transformation of these contaminants into more environmentally benign compounds [12–15].

In order to extend the scope of photocatalytic reactions at illuminated semiconductor powders as reported by Fox and co-workers [11], this paper is devoted to study the heterogeneous photocatalytic oxidation of some selected aryl alcohols by using TiO₂ powder (anatase), as a superior photocatalyst [16], in the presence of oxygen.

2. Experimental details

2.1. Materials

Titanium dioxide (Aldrich, anatase powder) was dried at 120 °C for 12 h in the oven and stored under nitrogen before use. Oxygen was dried by passage through a drying tube containing dry calcium chloride. Acetonitrile (Aldrich, HPLC grade) was distilled before use. Benzyl alcohol (1, Riedel-de Häen) was commercially available and was distilled before use. The substrates 1-phenylethanol (2), benzhydrol (3), 4-chlorobenzhydrol (4), hydrobenzoin (5), 4,4'-dichlorohydrobenzoin (6) and 4,4'-dimethoxyhydrobenzoin (7) were prepared via literature procedures and recrystallized before use [17,18].

2.2. Apparatus

A 450 W medium pressure Hg lamp (ACE Glass, immersion type) with a Pyrex well was used as the light source. Also, a 125 W medium pressure Hg lamp was used for kinetic studies of photocatalytic oxidation of benzyl alcohol. The system was covered with aluminum foil which served as light reflector and the apparatus was set up in a metallic cabinet.

IR spectra were done on Shimadzu-470 spectrophotometer using KBr-wafer technique. UV spectra were performed using Shimadzu UV 2101 PC UV–VIS scanning spectrophotometer. ¹H NMR were carried out using 90 MHz Varian 390 in CDCl₃ and TMS as an internal standard. Elemental analyses were determined using Perkin-Elmer

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elemental analyzer 240C. Melting points were measured on Mel-Temp-II melting points apparatus. TLC analyses were performed on (40 mm × 80 mm) precoated plastic sheets covered with a thin film of silica gel with fluorescent indicator. GC/MS analyses were carried out on a gas chromatography Hewlett-Packard HP 6890 using HP-5 (cross-linked 5% PHME siloxane) capillary column (30 m × 0.35 mm × 0.25 μm film thickness), Jeol TMS-600H.

Anodic potential was measured by cyclic voltammetry using glassy carbon electrode as a working electrode in 0.1 M KCl as supporting electrolyte [19].

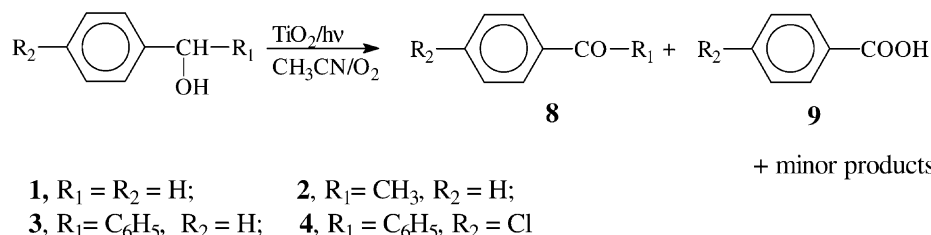
2.3. General procedure

A 400 ml solution (0.01 M) of the substrate (**1–7**) was prepared in dry acetonitrile to which 100 mg of TiO₂ (anatase) was added. The mixture was transferred to the reaction vessel, saturated by bubbling oxygen, sonicated using an

3. Results and discussion

The present article embraces photocatalysis of selected aryl alcohols (**1–7**) in the presence of aerated titanium dioxide (anatase) suspensions in anhydrous acetonitrile while purging with oxygen. A polar, nonhydroxylic solvent (CH₃CN) presents the best opportunity for controlling oxidative reactivity at the interface between a liquid reaction mixture and a solid irradiated photocatalyst [20]. Blank tests were performed in experimental conditions similar to those used for the photocatalytic oxidation experiments. No oxidation products were detected in the absence of catalyst and/or of light. Furthermore, experiments carried out in the absence of oxygen showed no significant evidence of product formation, confirming the essential role of oxygen for the photoreaction.

Results shown in Table 1 indicate that photocatalytic oxidation of compounds **1–4** gave mainly the corresponding aldehydes or ketones (**8**) and small amounts of acids (**9**).

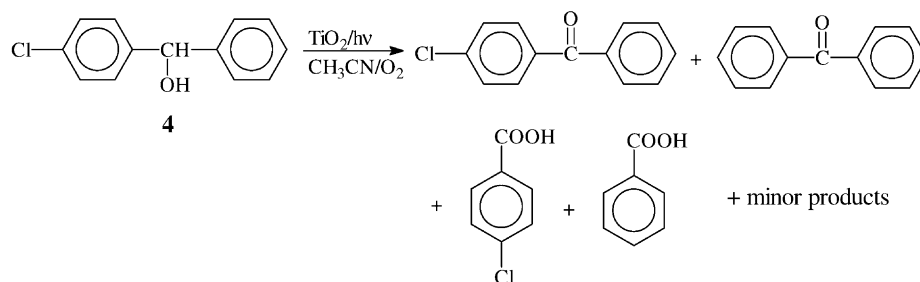


ultrasonic bath for 15 min and irradiated for the reaction period. The suspension composition was maintained by stirring with magnetic stirrer and by a slow stream of oxygen.

The reaction process was monitored by TLC. After the irradiation period, titanium dioxide was filtered using a medium porosity frit. The filtrate was concentrated by evaporation of the volatile solvent using rotatory evaporator and the resultant product mixture was analyzed using TLC, CC, and GC/MS techniques. Chemical yields of all products were determined by GC/MS analysis. Results are presented in Table 1.

The kinetics of photocatalytic oxidation of benzyl alcohol, as a model alcohol, was performed using 125 W Hg

For example, benzaldehyde was produced in 47.8% from oxidation of benzyl alcohol (**1**) in addition to the secondary oxidation product benzoic acid (28.8%). Acetophenone and benzophenone were formed in high yields (93.7 and 85.8%) along with small amounts of benzoic acid (1.5 and 2.4%) upon oxidation of 1-phenylethanol (**2**) and benzhydrol (**3**), respectively. The low yield of benzoic acid is understandable on the basis of the ease of oxidation of aldehydes compared to ketones. In case of 4-chlorobenzhydrol (**4**), 4-chlorobenzophenone (51%), 4-chlorobenzoic acid (16%), were obtained, in addition to benzophenone (13.1%) and benzoic acid (4.8%). Formation of the parent benzophenone and benzoic acid could be explained by oxidative dehalogenation under the reaction conditions.



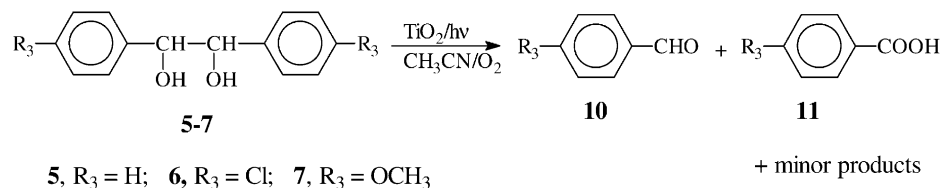
lamp. During the photoreaction, 1 ml of the slurry was withdrawn every 1 h using a syringe and after filtration, analyzed by HPLC technique, results are found in Figs. 1 and 2.

Furthermore, the study was also extended to include 1,2-diaryl alkane-1,2-diols. The hydrobenzoin **5–7** produced upon photocatalytic oxidation under the same condi-

Table 1
Photocatalytic oxidation products of 1–7

Compound no.	Substrate name	Time (h)	Conversion (%)	Products		
				Aldehydes or ketones (%)	Acids (%)	Other minor products (M^+ , m/e , %)
1	Benzyl alcohol	6.0	92	Benzaldehyde (47.8)	Benzoic acid (28.8)	Unknown (m/e 87, 8.1), (m/e 211, 7.31)
2	1-Phenylethanol	6.0	95	Acetophenone (93.7)	Benzoic acid (1.5)	Styrene 3.63; unknown (m/e 161.8, 1.1)
3	Benzhydrol	6.0	95	Benzophenone (85.8)	Benzoic acid (2.4)	Unknown (m/e 182, 4.4)
4	4-Chlorobenzhydrol	6.0	92	4-Chlorobenzophenone (51), benzophenone (13.1)	4-Chlorobenzoic acid (16), benzoic acid (4.8)	Unknown (m/e 280, 7.22)
5	Hydrobenzoin	8.0	90	Benzaldehyde (31.2)	Benzoic acid (38.7)	Acetamide 4.4; unknown (m/e 120, 3.1), (m/e 178, 11.1), (m/e 196, 11.6)
6	4,4'-Dichlorohydrobenzoin	8.0	90	4-Chlorobenzaldehyde (25.8), benzaldehyde (2.5)	4-Chlorobenzoic acid (58.2), benzoic acid (3.2)	Acetamide 6.1; unknown (m/e 193.8, 4.5), (m/e 180.8, 2.2), (m/e 154, 3.2)
7	4,4'-Dimethoxyhydrobenzoin	8.0	90	4-Methoxybenzaldehyde (64.7)	4-Methoxybenzoic acid (13.3)	Unknown (m/e 238, 0.1), (m/e 218, 12.0)

tions, a mixture of aldehydes (**10**) and acids (**11**) as major products, obviously through carbon–carbon scission of the radical cation.



It was observed that the UV absorption spectra of the target compounds have been undertaken to shed some light on their behavior upon irradiation. The maximum absorption of the investigated compounds (**1–7**) ranges between 217.8 nm for **2** and 281 nm for **7**, a range that will be cut-off by Pyrex glass (Table 2).

As the maximum emission of the used 450 W medium pressure mercury lamp ranges between 296.7 and 578.0 nm (4.18–2.15 eV), the obtained products are therefore originated through initial band gap excitation of TiO_2 (3.23 eV).

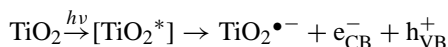
Cyclic voltammetric measurements using glassy carbon electrode revealed anodic potential of the model alcohol, benzyl alcohol, equals to +0.85 V which is less positive than the hole potential (+2.35 V), meaning that photocatalytic oxidation of benzyl alcohol is thermodynamically possible. Also, as the reduction potential of oxygen (−0.39 V) is less negative than the conduction band electron (−0.88 V), formation of the superoxide $\text{O}_2^{\bullet-}$ is thermodynamically allowed in the reaction medium.

4. Mechanistic aspects

In a photocatalytic process, the primary step following the radiation absorption by the photocatalyst is the generation

of electron–hole pairs which must be trapped in order to avoid recombination, i.e. charge separation is essential for

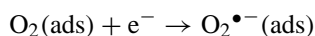
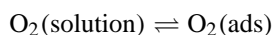
any photocatalytic electroprocess.



However, despite the contributions from a number of research groups, detailed mechanisms of the photocatalytic oxidation processes at the TiO_2 surface remain elusive for many important organic materials particularly regarding the initial steps involved in the radical reactions, which may involve one or more of the following radicals $\text{O}_2^{\bullet-}$, $\bullet\text{OH}$, $\text{HOO}\bullet$, $\text{Cl}\bullet$, etc. The use of nonaqueous reaction medium rules out the participation of hydroxy radicals, to be generated by water trapping of the hole, in the oxidation process [21].

It is useful to stress the point that in a photoreaction occurring on a semiconductor catalyst powder both the oxidation and reduction processes must occur on the same particle, although reaction sites for these processes may be different.

Adsorbed oxygen species are the traps for electrons according to the following equations:



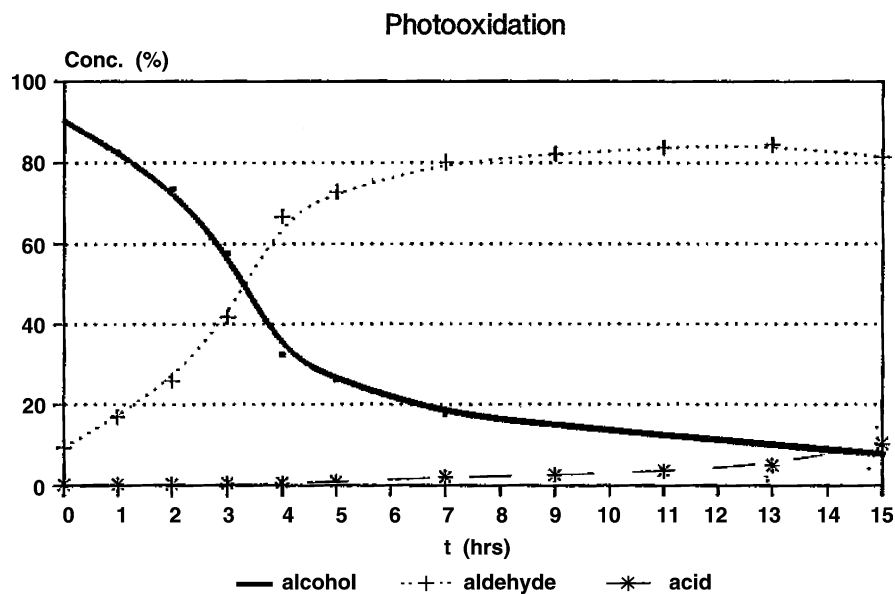


Fig. 1. Photocatalytic oxidation products of benzyl alcohol at different intervals.

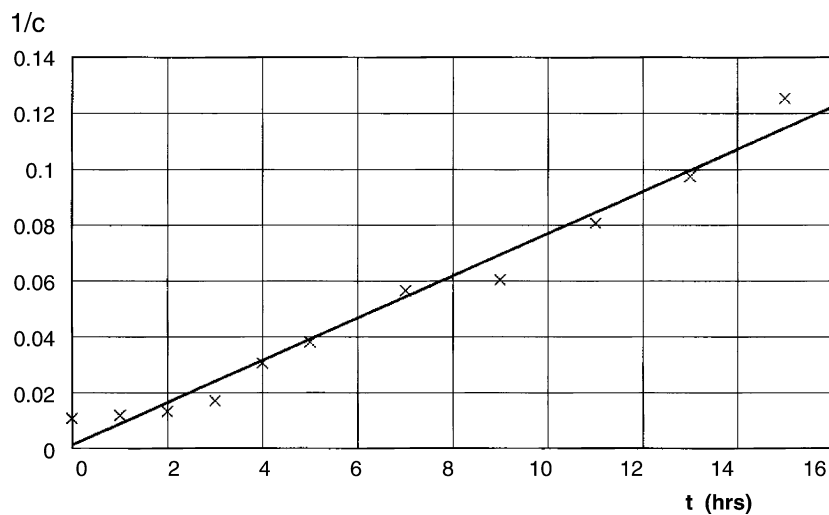
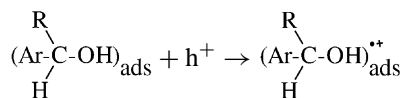
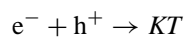
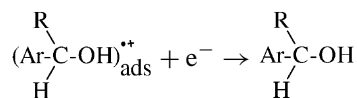
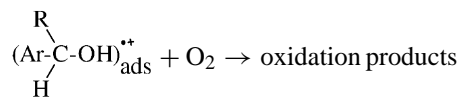
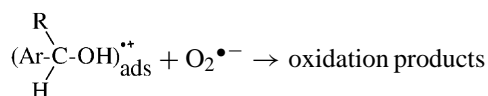


Fig. 2. Correlation of $1/c$ with time for photocatalytic oxidation of benzyl alcohol.

The adsorbed alcohol species in dry acetonitrile are the likely traps for holes forming the radical cation as follows:



The oxidation process takes place via interaction with the superoxide or oxygen accordingly:



5. Kinetics

The reaction pathway was also investigated through analysis of the products during the reaction progress at different

Table 2
UV spectra of 1–7

Compound no.	Compound name	UV spectra	
		λ_{max} (nm)	Absorbance
1	Benzyl alcohol	258.00	0.491
		219.00	1.802
2	1-Phenylethanol	263.60	0.200
		257.60	0.240
		252.20	0.198
		217.80	1.332
3	Benzhydryl	258.50	0.628
		225.50	2.778
4	4-Chlorobenzhydryl	257.60	0.290
		265.00	0.497
		259.80	0.536
		232.60	3.149
5	Hydrobenzoin	263.60	0.474
		258.00	0.599
		252.20	0.541
		224.20	2.678
6	4,4'-Dichlorohydrobenzoin	267.00	0.809
		233.00	3.219
7	4,4'-Dimethoxyhydrobenzoin	281.00	2.607
		273.80	3.036
		234.80	3.332

intervals. Contrary to Larson and Falconer, benzaldehyde and benzoic acid were found to be the main products. They reported that benzyl alcohol adsorbed on thin film TiO_2 catalyst is oxidized photocatalytically to benzaldehyde which eventually forms CO , CO_2 and water. Benzoic acid could not be detected in their study [22]. It can be noticed from the observation of the data reported in Fig. 1 that oxidation of benzaldehyde to benzoic acid starts to be significant only after almost complete disappearance of benzyl alcohol.

The rate determining step of the photocatalytic oxidation step is hypothesized to be the reaction between the superoxide ($\text{O}_2^{\bullet-}$) and the alcohol radical cation ($\text{ROH}^{\bullet+}$) over the catalyst surface. Accordingly, oxidation of the alcohol may be written in terms of Langmuir–Hinshelwood kinetics as

$$r = K''\theta_{\text{alc}}\theta_{\text{O}_2} \quad (1)$$

where K'' is the surface second-order rate constant, and θ_{alc} and θ_{O_2} are the fractional sites coverage by alcohol and oxygen [23], respectively.

$$\theta_{\text{alc}} = \frac{K_1 C_1}{1 + K_1 C_1} \quad (2)$$

$$\theta_{\text{O}_2} = \frac{K_2 C_2}{1 + K_2 C_2} \quad (3)$$

where K_1 and K_2 are the equilibrium adsorption constant of alcohol and O_2 , respectively.

The rate of benzyl alcohol photocatalytic oxidation, as a model alyl alcohol, has been studied and a second-order rate

constant for typical runs reports on a linear scale when the reciprocal of the measured concentration of benzyl alcohol ($1/C$) is plotted against irradiation time (t). Fig. 2 showed a line of slope $a = 1.325 \times 10^{-3} \text{ h}^{-1}$, intercept $b = 0.0075$, median = 0.0383, correlation coefficient = 0.98, and standard deviation = 0.03688.

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