



## Selective photooxidation of *ortho*-substituted benzyl alcohols and the catalytic role of *ortho*-methoxybenzaldehyde



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### ABSTRACT

It has been recently reported by Palmisano et al. (2015) [1] that the oxidation of 2-methoxybenzyl alcohol (2-MBA) to 2-methoxybenzaldehyde (2-MBAD) proceeds in water under near-UV light with an unexpected catalytic effect of 2-MBAD. In order to investigate the catalytic role of aldehyde in photolytic oxidation of *ortho*-substituted benzyl alcohols (OSBAs), reactivity runs were carried out with 2-methylbenzyl alcohol (2-MeBA), 2-nitrobenzyl alcohol (2-NBA), 2-hydroxybenzyl alcohol (2-HBA) and 2-chlorobenzyl alcohol (2-CIBA) in the absence and in the presence of their corresponding aldehyde. None of those alcohols showed a measurable oxidation rate even in the presence of their aldehydes but 2-NBA was oxidised very fast, although no corresponding carbonyl product was obtained. The possible catalytic role of 2-MBAD was investigated for the photolytic oxidation of 4-methoxybenzyl alcohol (4-MBA), 4-nitrobenzyl alcohol (4-NBA), 2-CIBA, 2-HBA, 2-MeBA and ferulic acid (FA). The results showed that 2-MBAD acts as a catalyst only for 4-MBA, 2-HBA and FA. The photocatalytic oxidation of OSBAs in the presence of powdered TiO<sub>2</sub> has been also carried out in order to investigate the mutual influences, if any, between homogeneous and heterogeneous processes. The reactivity runs were carried out with TiO<sub>2</sub> photocatalyst in water and under near-UV irradiation; a home-prepared (HP) TiO<sub>2</sub> sample was used along with Degussa P25. HP catalyst showed the best performance: the 2-MBA half-life time was 5 times smaller and the selectivity to aldehyde 13 times higher than in the presence of Degussa P25.

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### 1. Introduction

Heterogeneous photocatalysis publications works generally refer to waste water treatment to degrade harmful compounds such as pesticides, dyes, drugs, and their intermediates [2,3]. Photocatalytic reactions involve fast attacks of strong oxidizing agents, mainly hydroxyl radicals, which unselectively degrade and mineralize almost all organic compounds especially in water [4,5]. However, photocatalysis is capable also of selective oxidation and reduction to produce high value chemicals from a number of substrates [6–8].

Examples of selective heterogeneous photocatalytic reactions are the syntheses of cyclic amino acids [9], cyclohexanol and

cyclohexanone [10], imines [11], 1- and 2-adamantanol and adamantanone [12], and some heterocyclic and aromatic aldehydes [7,13].

Homogeneous photocatalysis has been also deeply investigated during the last decades for carrying out reactions such as water splitting, degradation of harmful contaminants and organic syntheses [14–20]. On the last field, however, a limited number of studies on the selective oxidation of alcohols has been done, although this photoreaction has been deeply investigated in heterogeneous systems containing TiO<sub>2</sub>-based catalysts [13,21–23].

Homogeneous systems, such as ruthenium complexes [24] or ferric ions [25–27], have been used as photocatalysts too. Chen et al. [24] reported that the photocatalytic oxidation of aliphatic and aromatic alcohols under sun light in water at ambient conditions produces aldehydes and ketones with high selectivity by using a chromophore–catalyst dyad assembly of ruthenium

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polypyridyl complexes. Spasiano et al. [25] carried out the photosynthesis of benzaldehyde from benzyl alcohol in water by using Fe(III) aquo-complex as photocatalyst at very low pH (0.5) and high yield values in aldehyde were obtained. Benzyl alcohol was also oxidised to benzaldehyde under visible light irradiation by using homogeneous  $\text{CuCl}_2/\text{solvent}$  as catalyst and molecular oxygen as oxidant [28]. The obtained results showed that the formation of a visible light responsive complex between Cu(II) and the solvent is responsible for the benzyl alcohol partial oxidation; molecular oxygen is not incorporated into benzaldehyde and it is only involved in the Cu(I) oxidation into Cu(II), serving as a terminal hydrogen acceptor to form  $\text{H}_2\text{O}$ .

Selective photolytic and photocatalytic reactions could offer alternative green routes to organic syntheses that currently are carried out under environmentally unfriendly conditions: high temperature and pressure, and the use of dangerous reactants and organic solvents [7,21].

A recent publication [1] reported an unexpected autocatalytic photooxidation of 2-methoxybenzyl alcohol (2-MBA) in water, under UV light and without any catalyst. The main oxidation product was the corresponding aldehyde, 2-methoxybenzaldehyde (2-MBAD), which also had the role of catalyst. The highest selectivity for 2-MBAD production from 4-MBA oxidation in the presence of 20%  $\text{O}_2$  (air) was 85% for 70% conversion (64% yield). Indeed, it has been showed that, only in presence of oxygen and 2-MBAD, such reaction takes place at a measurable rate. The effect of the concentration of dissolved oxygen in water was also investigated: the molecular oxygen affects the reaction rate in an ambivalent role that has never been seen in analogous photooxidations of aromatic alcohols. Oxygen is in fact necessary for the reaction to take place, but it is detrimental in high concentrations due to its quenching role. In the same study [1] other aromatic alcohols, in addition to 2-MBA, were also tested for a preliminary investigation on the correlation between structural features and autocatalytic behaviour of their corresponding aldehyde. Thus, benzyl alcohol, 3-methoxybenzyl alcohol, 4-methoxybenzyl alcohol, 2,4-dimethoxybenzyl alcohol, and 2,3,4-trimethoxybenzyl alcohol were tested by following the same procedure used for 2-MBA; only for 2,4-dimethoxybenzyl alcohol, the corresponding aldehyde showed a similar behaviour to that observed for 2-MBAD in the 2-MBA oxidation.

The present study has been devoted to understand if the photoreactivity features observed with the 2-MBA could be extended to other *ortho*-substituted benzyl alcohols (OSBAs). To this aim, 2-methylbenzyl alcohol (2-MeBA), 2-hydroxybenzyl alcohol (2-HBA), 2-chlorobenzyl alcohol (2-CIBA), and 2-nitrobenzyl alcohol (2-NBA) have been tested for photooxidation in homogeneous phase in the presence of their corresponding aldehydes. Moreover, the possible role of 2-MBAD as homogeneous catalyst has been studied in the oxidation of 4-methoxybenzyl alcohol (4-MBA), 4-nitrobenzyl alcohol (4-NBA), 2-CIBA, 2-HBA, 2-MeBA and ferulic acid (FA). Finally, in order to investigate likely influences between homogeneous and heterogeneous photocatalytic systems, the OSBAs have been photooxidized in aqueous suspensions containing powdered commercial and home-prepared  $\text{TiO}_2$ . Hereafter, the aldehydes corresponding to the OSBAs are indicated as follows: 2-methylbenzaldehyde (2-MeBAD), 2-hydroxybenzaldehyde (2-HBAD), 2-chlorobenzaldehyde (2-CIBAD), and 2-nitrobenzaldehyde (2-NBAD).

## 2. Experimental

### 2.1. Catalyst preparation

The experimental details of home-prepared  $\text{TiO}_2$  have been reported elsewhere [26]. The precursor solution was obtained by

adding 20 mL of  $\text{TiCl}_4$  (purity >97%, Fluka) dropwise under magnetic stirring to 200 mL of deionized water contained in a 500 mL beaker placed inside an ice bath. After that, the beaker was sealed and mixing was prolonged for 12 h at room temperature, eventually obtaining a clear solution. 125 mL of the resulting solution was poured inside a 250 mL round-bottomed flask fitted with a Graham condenser. The flask was heated at 373 K, magnetically stirred, and refluxed for 2 h; the reflux zero time has been taken as that for which the solution left its transparency. The obtained suspension was then dried at 323 K by means of a rotary evaporator machine (Buchi, model M) working at 100 rpm in order to obtain the final powdered catalysts. The so prepared catalyst is hereafter indicated as HP.

Previous characterizations of HP and Degussa P25  $\text{TiO}_2$  [29,30] showed that HP catalyst is constituted by anatase (ca. 4%), rutile (ca. 1.4%) and amorphous phases (ca. 95%) while, for the commercial one, these percentages are 72, 18 and 10%, respectively. BET surface areas of Degussa P25 and HP are  $50 \text{ m}^2/\text{g}$  and  $226 \text{ m}^2/\text{g}$ , respectively; primary and secondary particle sizes of HP are 3–7 nm and 25 nm and those of P25 are 30 and 80 nm, respectively.

### 2.2. Reaction system a (annular photoreactor)

A Pyrex batch home-made photoreactor of cylindrical shape (internal diameter: 100 mm; height: 126 mm) was used for carrying out reactivity runs in homogeneous and heterogeneous regimes with the following substrates: 2-methylbenzyl alcohol (2-MeBA), 2-hydroxybenzyl alcohol (2-HBA), 2-chlorobenzyl alcohol (2-CIBA) and 2-nitrobenzyl alcohol (2-NBA). For the sake of comparison the previously investigated 2-methoxybenzyl alcohol (2-MBA) [1] was also tested. The reacting system set up is reported in Fig. S1; the photoreactor was supplied with ports in its upper section for the inlet and outlet of gases and for sampling. The aqueous solution or suspension (volume of 800 mL) was magnetically stirred and an  $\text{O}_2/\text{N}_2$  mixture with different  $\text{O}_2$  concentrations was bubbled inside. These mixtures were set by means of a Bronkhorst high-tech mass flow controller. The bubbling started 30 min before switching the lamp on and it was maintained during all the runs. The dissolved  $\text{O}_2$  concentration was measured before starting the irradiation by using an HD22559.2 apparatus (Delta Ohm). When pure oxygen was bubbled, the measured concentration in water was 1.2 mM; this figure linearly decreased with the decrease of  $\text{O}_2$  percentage in the bubbled mixture as expected by Henry's law. A 125 W medium pressure Hg lamp (Helios Italquartz, Italy; its spectrum is shown in Fig. S2) was axially positioned inside the photoreactor and it was cooled by water circulating through a Pyrex thimble (external diameter: 36 mm). The radiation energy impinging on the solution or suspension had an average value of  $4.4 \text{ mW}\cdot\text{cm}^{-2}$ ; it was measured between 315 and 400 nm by using a radiometer (Delta Ohm, DO 9721). During the photoreactivity runs the aqueous solution or suspension reached the temperature of ca. 300 K. For all the runs the initial alcohol concentration was 0.5 mM; when the *ortho*-substituted benzaldehyde (OSBAD) corresponding to the tested alcohol was added to the solution, its concentration was 0.165 mM.

For the heterogeneous runs, commercial  $\text{TiO}_2$  (Degussa P25) and HP  $\text{TiO}_2$  were used in suspension at the same experimental conditions used for the homogeneous runs. The amount of both catalysts was chosen in such a way that the resulting suspension could transmit only 10% of the total irradiation measured at the outer wall of photoreactor in the presence of only water. This strategy guaranteed that all the catalyst particles were irradiated.

During the photoreactivity runs, samples were withdrawn at fixed times. In the case of heterogeneous runs these samples were immediately filtered through a  $0.45 \mu\text{m}$  hydrophilic membrane

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